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RECOVERY AND INTERNAL OXIDATION
OF
COLUMBIUM AND COLUMBIUM ALLOYS

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LOCKHEED MISSILES & SPACE COMPANY

TECHNICAL REPORT AFML-TR-66-253

NOVEMBER 1966

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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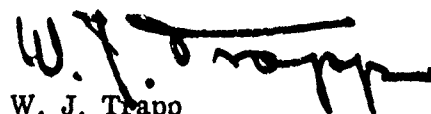
LOCKHEED MISSILES & SPACE COMPANY

FOREWORD

This report was prepared by Lockheed Missiles & Space Company under USAF Contract No. AF 33(657)-10281. The contract was initiated under Project No. 7351, "Metallic Materials," Task No. 735106, "Behavior of Metals." The project was administered by the Air Force Materials Laboratory, Research and Technology Division with Mr. F. G. Ostermann acting as Project Engineer.

The work covered by this report was conducted from 30 March 1964 to 30 March 1966. This study was initially directed toward an investigation of the recovery behavior of high-purity columbium, Cb-1 at. % W, Cb-1 at. % Zr and Cb-1 at. % W-1 at. % Zr. Subsequently, the program was extended to include a study of the internal oxidation of the four test materials. In particular, emphasis was placed on a study of the precipitates formed in the Cb-1W-1Zr alloy upon internal oxidation and the resulting mechanical behavior of this alloy at ambient and elevated temperatures.

Acknowledgment is made to W. C. Coons for development of metallographic techniques for revealing dislocation substructures in the Cb-1W-1Zr samples, and to L. C. Potter for assistance in the mechanical testing.

Manuscript released by authors 31 August 1966 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

W. J. Trapp
Chief, Strength and Dynamics Branch
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Air Force Materials Laboratory

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ABSTRACT

The effects of recovery and internal oxidation treatments on high-purity columbium, Cb-1W, Cb-1Zr, and Cb-1W-1Zr alloys were investigated in terms of tensile properties. Dislocation arrangements developed in the ternary alloy were examined by thin film transmission electron microscopy. The tensile properties of the Cb-1W-1Zr at room temperature, creep properties at 1200°C, and the recrystallization temperature were determined for the alloy after various treatments.

The recovery behavior of the unalloyed columbium was comparable to that of the Cb-1W alloy. However, the two alloys containing zirconium showed somewhat different behavior due to hardening which was thought to be a result of an interaction between the zirconium atoms and oxygen impurities present in the original sheet.

Transmission electron microscopy revealed that precipitates develop at dislocations during internal oxidation of Cb-1W-1Zr at 800°C for times in excess of 20 hr. In the as-recrystallized alloy, internal oxidation for 100 hr at 800°C produced an extremely high density of coherent zones, while at 900°C larger zones were produced. Zones produced at 800°C were not stable at 1200°C where large precipitates of monoclinic zirconium oxide were produced.

The yield and ultimate tensile strengths of recrystallized Cb-1Zr and Cb-1W-1Zr were doubled by internal oxidation treatments at 800°C. In this condition the creep rupture life of the ternary alloy at 1200°C was twenty times that of the as-recrystallized alloy. For short time tests at 1200°C, the recovered Cb-1W-1Zr alloy showed a higher creep resistance than the alloy in the strained or recrystallized conditions.

Structures developed in the Cb-1W-1Zr alloy by internal oxidation were found to be more effective in raising the recrystallization temperature than those developed by recovery treatments.

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ILLUSTRATIONS

Section 1
INTRODUCTION

Pure metals are soft because glissile dislocations can move through the lattice in a relatively unhindered manner. Pure metals can be hardened by alloying and by introducing other barriers to dislocation motion. Such barriers are dislocations produced by cold work, which can interact with each other and effectively prevent further deformation until the stress is raised. Resistance to slip can also be imparted by dispersing a fine precipitate or second phase throughout the lattice.

During annealing, cold-worked metals soften as a result of the rearrangement of dislocations into low-energy boundaries and networks. Depending upon the specific recovery treatment, this rearrangement can result in stable dislocation configurations which give the material superior mechanical properties at elevated temperatures. The effectiveness of a dispersed phase in strengthening a metal at elevated temperatures is dependent upon many factors, among which are the stability of the particular phase and the influence the dispersed phase has on further stabilizing the dislocation substructure.

Columbium is notable as the first BCC metal in which stacking faults were observed.[1] However, in subsequent electron microscope studies[2-4] partial dislocations have not been observed in columbium, and the dislocation structures seen after deformation at room temperature indicate that cross slip is a very easy process. Work on electron-beam melted columbium[4] prestrained 8% at room temperature indicated that dislocation networks were formed during the early stages of recovery at 900°C. After longer recovery times (> 25 hr) some fine precipitates were observed on dislocations outside the networks, which resulted in detectable hardening. It was concluded that these precipitates were formed at favorable sites from impurities present in the original recrystallized sheet.

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A hardening effect was found in columbium and to a greater extent in Cb-1Zr after annealing at elevated temperatures [5] In the alloy the effect was attributed to the formation of zirconium oxide precipitates. These precipitates were also thought responsible for the observed increase in recrystallization temperature. [5] Other work on Cb-1Zr [6] indicated the presence of several crystalline forms of zirconium oxide produced upon annealing for 1 hr at temperatures up to 1760°C. These workers also revealed an aging effect in this alloy by determining hardness at room temperature as a function of aging time at 925°C. The absorption of interstitial impuritie· and the consequent hardening effect in columbium and its alloys can largely be eliminated by wrapping in foil during annealing. [7] These results suggest a method of controlled strengthening of columbium-zirconium alloys which has hitherto received only a cursory examination.

In the present study of high purity columbium, Cb-1 at. % W, Cb-1 at. % Zr, and Cb-1 at. % W-1 at. % Zr, the initial object was to strengthen the materials by creating dislocation configurations (through prestrain and recovery treatments) which would resist slip and be thermally stable. During the work it became apparent that interstitials, particularly oxygen, were being absorbed during annealing and that under certain conditions the magnitude of the associated strengthening effect could be very large. The overall program was therefore modified to include parallel studies on the recovery behavior of the four test materials (foil wrapped) and on the influence of internal oxidation as a result of vacuum annealing the materials in the unwrapped condition.

Section 2
EXPERIMENTAL PROCEDURE

2.1 TEST MATERIALS

High-purity columbium and three columbium-base alloys — Cb-1 at.% W, Cb-1 at.% Zr, and Cb-1 at.% W-1 at.% Zr — were employed in this investigation. All four materials were produced by Wah Chang Corporation from vacuum arc-melted castings of an electron-beam melted columbium ingot. Chemical analyses of the final arc-melted castings were made by Wah Chang Corporation and are listed in Table 1. The test materials were supplied by Wah Chang Corporation as 0.040-in.-thick sheet in approximately an 80% cold-rolled condition. The analyses of interstitial elements in the final rolled sheet are given in Table 2, as provided by the producer.

Tensile and creep-rupture specimens were machined with their axes in the rolling direction of the sheet. The geometry of the specimens is shown in Fig. 1. To eliminate any possible surface contamination, the samples were chemically polished in a solution of 17% hydrofluoric acid, 17% nitric acid, 66% water, removing approximately 0.0005-in. from each surface.

Recrystallization treatments were selected to produce nearly equal grain sizes for the different alloys. All test specimens were recrystallized in a Brew vacuum furnace which maintained maximum pressures of 10^{-5} torr at the recrystallization temperatures. Temperatures were measured and controlled within $\pm 1C°$ by a Pt/Pt-10% Rh thermocouple. Ten specimens in intimate contact with each other were recrystallized at one time. The control thermocouple was spot welded directly to the shoulder of an outside specimen. The recrystallization teatments and resulting average grain diameters are given below for each test material.

Material	Temperature (°C)	Time (hr)	Average Grain Diameter (mm)
Cb	1050	1	0.022
Cb-1Zr	1200	1	0.017
Cb-1W	1400	1	0.022
Cb-1Zr-1W	1400	1	0.016

Chemical analyses of the recrystallized materials showed that no increase in interstitial content had occurred.

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Table 1

CHEMICAL ANALYSES OF ARC-MELTED CASTINGS OF COLUMBIUM TEST MATERIALS

	Composition (wt. %)			
Element	Columbium	Cb-1W	Cb-1Zr	Cb-1W-1Zr
C	0.0030	0.0040	<0.0030	<0.0030
O	0.0055	0.0090	<0.0050	0.0115
N	0.0020	0.0040	0.0040	0.0030
H	0.0004	0.0004	0.0003	0.0004
W	0.0045	1.96 (1.0 at. %)	0.0020	1.84 (0.94 at. %)
Zr	0.0100	0.0375	0.93 (0.95 at. %)	0.96 (0.99 at. %)
Cb	Balance	Balance	Balance	Balance
Ta	<0.05	<0.05	<0.05	<0.05
Al	<0.0020	<0.0020	<0.0020	<0.0020
B	<0.0001	<0.0001	<0.0001	<0.0001
Cd	<0.0005	<0.0005	<0.0005	<0.0005
Co	<0.0010	<0.0010	<0.0010	<0.0010
Cr	<0.0020	<0.0020	<0.0020	<0.0020
Cu	<0.0040	<0.0040	<0.0040	<0.0040
Fe	<0.0050	<0.0050	<0.0050	<0.0050
Mg	<0.0020	<0.0020	<0.0020	<0.0020
Mn	<0.0020	<0.0020	<0.0020	<0.0020
Mo	<0.0020	<0.0020	<0.0020	<0.0020
Ni	<0.0020	<0.0020	<0.0020	<0.0020
Pb	<0.0020	<0.0020	<0.0020	<0.0020
Si	<0.0050	<0.0050	<0.0050	<0.0050
Sn	<0.0010	<0.0010	<0.0010	<0.0010
Ti	<0.0040	<0.0040	<0.0040	<0.0040
V	<0.0020	<0.0020	<0.0020	<0.0020
Hf	<0.0080	<0.0080	<0.0080	<0.0080

Table 2

INTERSTITIAL ANALYSES OF THE FINAL SHEET TEST MATERIALS

Element	Columbium	Composition (ppm)		
		Cb-1W	Cb-1Zr	Cb-1W-1Zr
C	<30	< 30	40	50
N	45	45	40	60
O	70	120	140	150
H	2	2	2	2

2.2 FLOW-STRESS RECOVERY

2.2.1 Flow-Stress Recovery Measurements

All flow-stress recovery tensile tests were performed at room temperature on an Instron Testing machine at a strain rate of 0.03 per min. Extensometers, employing dual LVDT's, provided a continuous measurement of strain. The extensometer output was amplified within the Instron so that load-elongation curves were autographically recorded in each test. The resulting least count for load was 10 lb, and the least count for strain was 0.002.

2.2.2 Recovery Treatments

Following a 10% tensile strain, the four columbium materials were given recovery anneals at 800, 900, or 1000°C at a pressure of 2×10^{-6} torr in the Brew vacuum furnace. Annealing times were 1, 4, 16.5 or 20, and 100 hr. After completion of the annealing treatments, the tensile specimens were restrained at room temperature until maximum load was achieved. After the 100-hr treatment at 800°C, the two alloys containing zirconium exhibited a substantial increase in strength. This strengthening effect suggested that interstitial elements were being picked up during the longer vacuum annealing treatments. To verify this conjecture a second series of anneals was performed for 100 hr at 800°C on the four prestrained columbium sheet materials with the samples wrapped in a double layer of 0.002-in.-thick molybdenum foil. Molybdenum was chosen because it has been demonstrated to provide effective protection
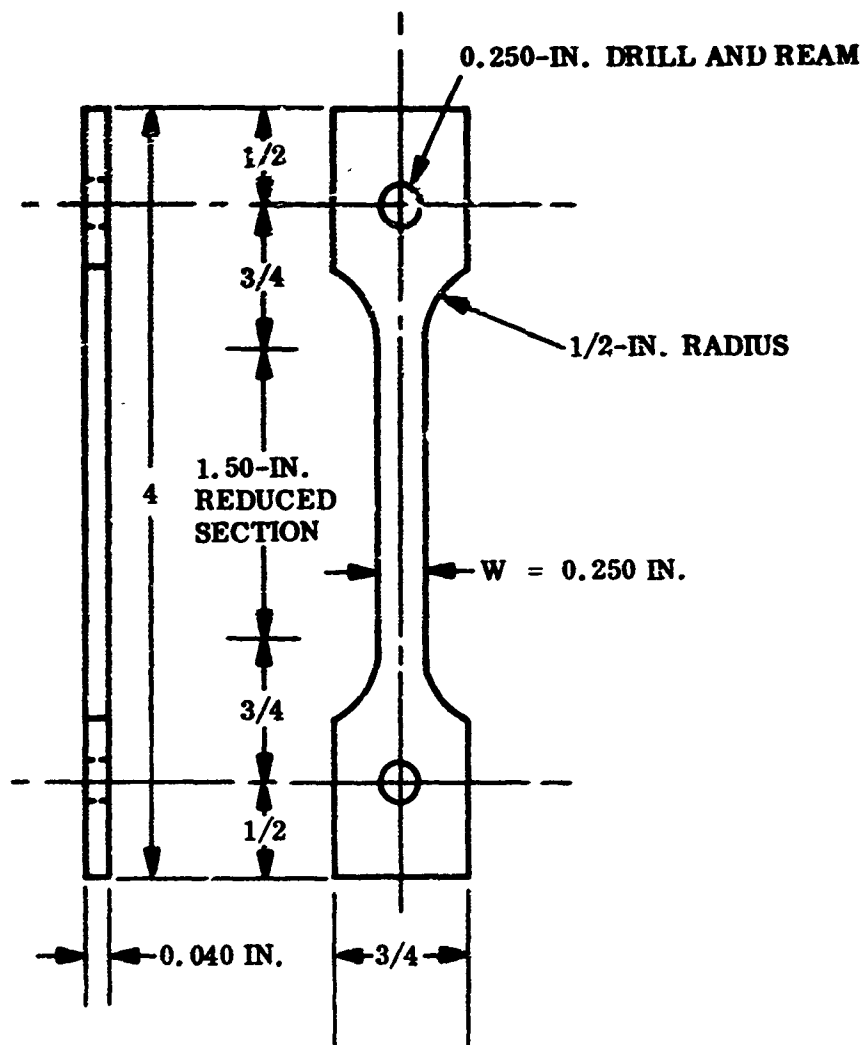
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0.250-IN. DRILL AND REAM

1/2

3/4

1.50-IN.
REDUCED
SECTION

4

1/2-IN. RADIUS

W = 0.250 IN.

3/4

1/2

0.040 IN.

3/4

Fig. 1   Tensile and Creep-Rupture Test Specimen Design

against the absorption of interstitial elements by columbium and its alloys.[7] Upon retesting these samples, no strengthening effect was found, which supported the idea that interstitial elements absorbed during annealing were responsible for the strengthening initially observed in the alloys containing zirconium.

To determine the extent and type of interstitial pickup which may have occurred, samples of each of the four columbium sheet materials which were annealed at 800°C for 100 hr both in the wrapped and unwrapped condition, were analyzed at Wah Chang Corporation for carbon, hydrogen, oxygen, and nitrogen. The results of these analyses are listed in Table 3. These results show conclusively that carbon and oxygen levels significantly increased during annealing for 100 hr at 800°C without foil protection. Oxygen pickup was significantly greater than that for carbon, the increase being about 200 ppm for unwrapped Cb-1Zr and about 350 ppm for unwrapped Cb-1W-1Zr. The unwrapped columbium and Cb-1W alloy absorbed 50 and 90 ppm oxygen, respectively. The columbium sheet materials which were foil wrapped did not absorb any appreciable amounts of interstitial contaminants.

Table 3

INTERSTITIAL ANALYSES OF COLUMBIUM SHEET MATERIALS AFTER
ANNEALING AT 800°C FOR 100 HOURS IN
THE WRAPPED AND UNWRAPPED CONDITIONS

	Columbium		Cb-1W		Composition (ppm) Cb-1Zr		Cb-1W-1Zr	
Element	Wrapped	Unwrapped	Wrapped	Unwrapped	Wrapped	Unwrapped	Wrapped	Unwrapped
C	40	50	30	50	40	70	50	80
N	22	27	42	42	34	31	35	52
O	60	120	110	210	80	330	110	510
H	3	3	2	2	3	3	3	2

Since wrapping has been demonstrated to effectively eliminate interstitial contamination during the annealing treatments, it is possible to study the recovery behavior of these four alloys using this technique. Thus, for studying the recovery behavior of the four test materials all specimens were wrapped in a double layer of 0.002-in.-thick

molybdenum foil. Also, all four test materials were given equivalent annealing treatments in the unwrapped condition to determine the degree of strengthening which occurred as a result of interstitial contamination.

In addition, a number of as-recrystallized specimens of Cb-1W-1Zr alloy were annealed unwrapped at 800°C for 16.5 and 100 hr, to explore more fully the strengthening effect. The true stress — true strain characteristics of this alloy were determined at room temperature using the procedures previously described.

To distinguish between the different annealing treatments performed on the columbium sheet materials, the following notation will be used in this report. The term "recovery" will be used to refer to annealing treatments where the specimens were wrapped in molybdenum foil, while the term "internal oxidation" will be used to describe treatments where the specimens were not protected from interstitial absorption by foil wrapping.

2.2.3 Method of Evaluating Flow-Stress Recovery

Recovery behavior was primarily measured in terms of the decrease of flow stress after various recovery treatments, similar to the technique used in previous studies.[4, 8] The effect of a recovery anneal on the true stress — true strain curve is shown schematically in Fig. 2. The degree of recovery is evaluated in terms of the fractional flow-stress recovery parameter, f_r. This parameter is defined as the decrease in the flow stress due to the recovery treatment divided by the decrease experienced if the material recovered completely to the flow stress of the recrystallized material. Thus, as illustrated in Fig. 2

$$f_r = \frac{\sigma_1 - \sigma_2}{\sigma_1 - \sigma_y}$$

The portion of the prestrain curve that represented homogeneous flow was extrapolated to 1.0% strain to obtain the σ_y value. This extrapolation was made by drawing a

$$f_r = \frac{(\sigma_1 - \sigma_2)}{(\sigma_1 - \sigma_y)}$$
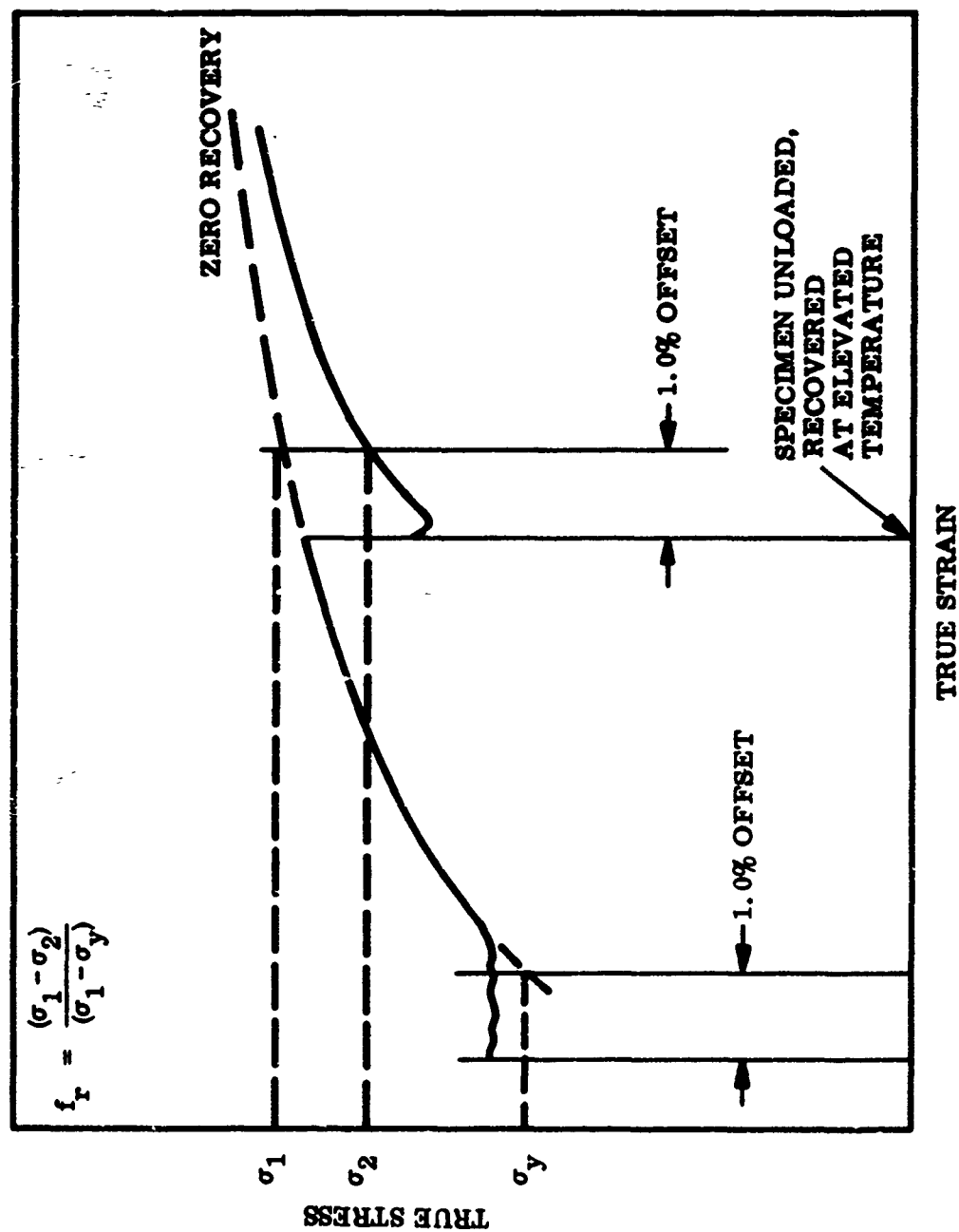
Fig. 2   Schematic Diagram Showing Method Used to Evaluate Degree of Recovery for Materials Which Exhibit Discontinuous Yielding

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straight line through the flow-stress data plotted as log stress versus log strain. After annealing, all of the tensile samples exhibited homogeneous deformation or nonhomogeneous deformation of such short duration that the above extrapolation was not required to obtain the value of σ_2.

2.3 EFFECT OF PRIOR RECOVERY OR INTERNAL OXIDATION ON CREEP-RUPTURE BEHAVIOR OF THE Cb-1W-1Zr ALLOY

Constant load creep-rupture tests were performed on the Cb-1W-1Zr alloy at a temperature of 1200°C and at two values of stress, viz., 9000 and 13,000 psi. Tests were performed on an A'c-Weld creep testing machine using the Brew vacuum furnace. Pressures during creep testing were maintained at values less than 10^{-5} torr. To minimize oxygen pickup during creep testing, a 0.002-in.-thick molybdenum foil sleeve was placed around the reduced section of the specimens. Specimens were heated and held at the test temperature for 5 min prior to loading. Elongation during test was measured by means of a dial gage (0.001 in. divisions) mounted on the lower pull-rod linkage. Strain readings were not made directly on the reduced section during the creep test. However, measurements on gage marks on the reduced section made before test, at various times on interrupted tests, and after rupture, all agreed very closely with the pull-rod dial gage readings. The Cb-1W-1Zr alloy specimens were in one of the following five conditions prior to creep testing: (1) as-recrystallized, (2) prestrained 10%, (3) prestrained-recovered at 800°C for 100 hr, (4) prestrained-internally oxidized at 800°C for 100 hr, and (5) internally oxidized at 800°C for 100 hr.

2.4 ELECTRON MICROSCOPY

Direct transmission electron microscopy was carried out on thin foils produced by a two stage polishing technique. Tensile samples, which were initially 0.040-in.-thick, were chemically polished to approximately 0.004 in. using a solution of 50 parts hydrofluoric and 50 parts nitric acid at a temperature of approximately 60°C. Polishing was continued until small perforations appeared in the sample. Final thinning was accomplished in a solution of 50 parts lactic acid, 25 parts hydrofluoric acid and

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25 parts sulfuric acid, at a potential of 12 V. The solution was stirred and maintained at a temperature between 40°C and 60°C. The foils were examined in a Hitachi HU 11 electron microscope operating at 100 kV.

Dislocation substructures developed during recovery and internal oxidation of the Cb-1W-1Zr alloy were observed after prestraining 10% at room temperature and annealing at 800°C for 1, 20, and 100 hr.

Some studies of dislocation arrangements formed during creep-rupture tests at 1200°C were also made on the same alloy. Tests were interrupted during the steady-state and tertiary creep regions at 2% and 9% creep strain, respectively, for specimens tested after the following treatments: (1) prestrained – recovered at 800°C for 100 hr, (2) prestrained – internally oxidized at 800°C for 100 hr.

To investigate the phenomenon of hardening during annealing of unwrapped Cb-1W-1Zr alloy, as-recrystallized specimens were internally oxidized at 800°C and 900°C for 100 hr and thin foils prepared and examined. In addition, some thin foils were taken from specimens internally oxidized at 800°C for 100 hr and then exposed at 1100°C for 1 hr.

2.5 EFFECT OF PRIOR RECOVERY OR INTERNAL OXIDATION ON THE RECRYSTALLIZATION BEHAVIOR OF THE Cb-1W-1Zr ALLOY

After receiving a 10% prestrain, a number of Cb-1W-1Zr tensile specimens were either recovered or internally oxidized at 800°C for 100 hr at 10^{-6} torr. Specimen blanks (0.2 in. × 0.25 in. × 0.040 in.) were then cut with an abrasive wheel from the gage sections of the as-prestrained and prestrained and heat-treated tensile specimens. One hour annealing treatments at 1350, 1400, 1450, 1500, and 1550°C were performed on samples wrapped in foil for each of the conditions described above. Columbium foil (0.001-in.-thick) was used for wrapping, due to difficulties encountered in trying to wrap the small package of samples with the thicker molybdenum foil.

Rockwell hardness measurements (15-T scale) were obtained for each of the specimens before and after annealing. Following the annealing treatments, metallographic examinations were performed on each of the specimens. The samples were taken through the following steps prior to examination:

(1) Mounted in bakelite and hand ground through 600 grit SiC papers
(2) Polished automatically using 1 μ diamond paste
(3) Polished automatically using "Cer-Cre" polishing compound
(4) Etched for 2 hr by immersion in a solution containing 7.5 ml hydrofluoric acid, 2.5 ml nitric acid, and 100 ml water

Section 3

RESULTS AND DISCUSSION

3.1 RECOVERY AND INTERNAL OXIDATION OF PRESTRAINED COLUMBIUM AND COLUMBIUM ALLOYS

3.1.1 Effect of Recovery on Flow-Stress

The flow-stress recovery of high-purity columbium, Cb-1W, Cb-1Zr, and Cb-1W-1Zr alloys was studied at 800, 900, and 1000°C. The room temperature stress-strain curves of the high-purity columbium and the Cb-1W alloy for various recovery times at 900°C are shown in Figs. 3 and 4, respectively.

The form of the stress-strain curves is very similar for the two materials. However, at any particular value of strain the strength of the Cb-1W is between 30 to 50% greater than that of the high-purity columbium. Another feature to note in the stress-strain curves in Figs. 3 and 4 is the increasing yield drop obtained with increasing recovery time. This behavior was more pronounced for recovery at 1000°C, but was not evident at all for 800°C recovery. In general, the same behavior was observed for high-purity columbium in an earlier study of flow-stress recovery.[4] Some form of strain-aging apparently occurs which is more pronounced at the higher recovery temperatures. Oxygen is thought to make the largest contribution to the strain-aging effect. This point will be discussed in greater detail later in this section.

It is also of interest to note that upon restraining the recovered materials, the strengths developed at large strains will exceed those achieved in the as-recrystallized condition, at least for the shorter recovery times. This is a result of the initial higher rate of work hardening after recovery.
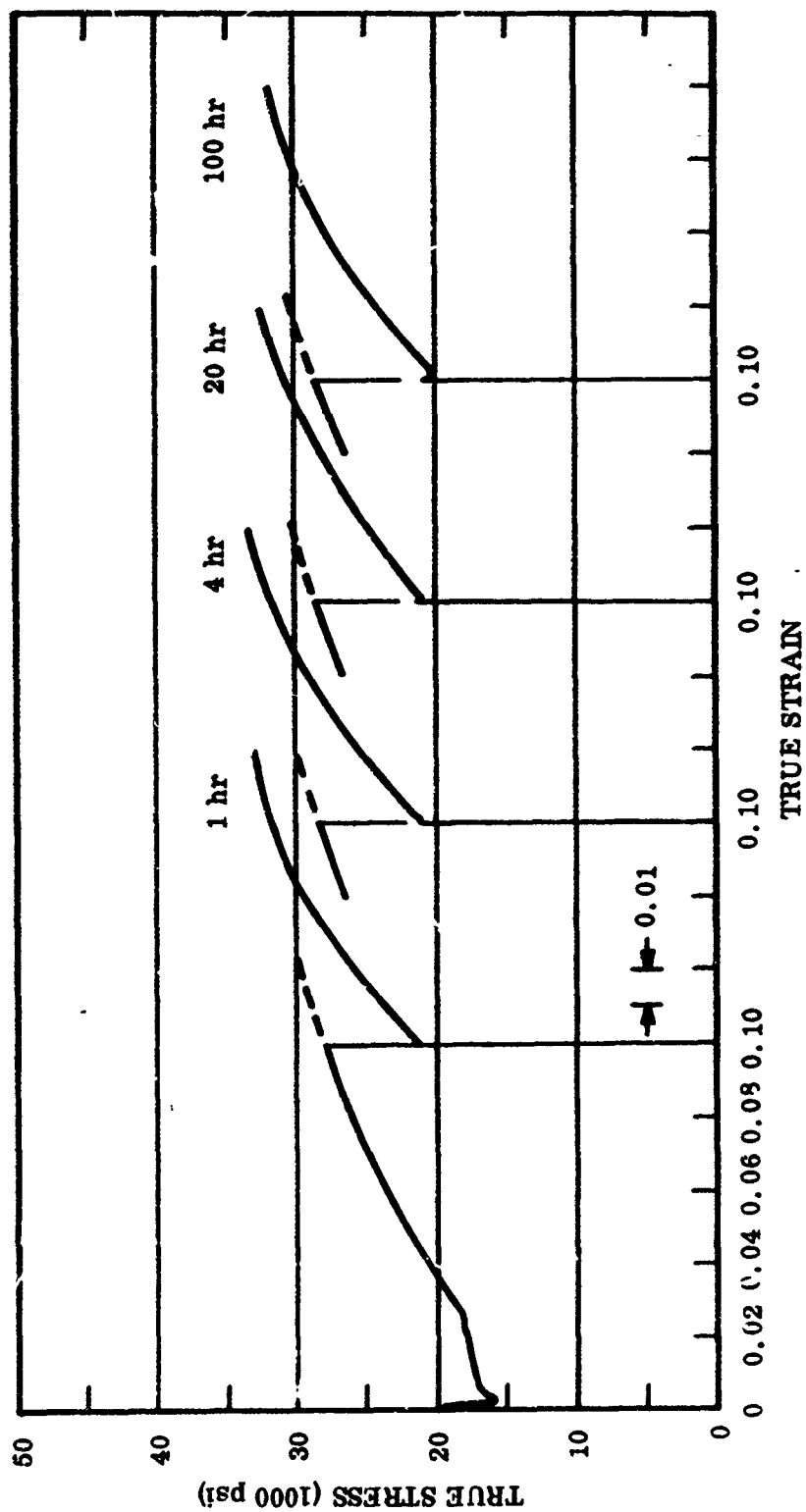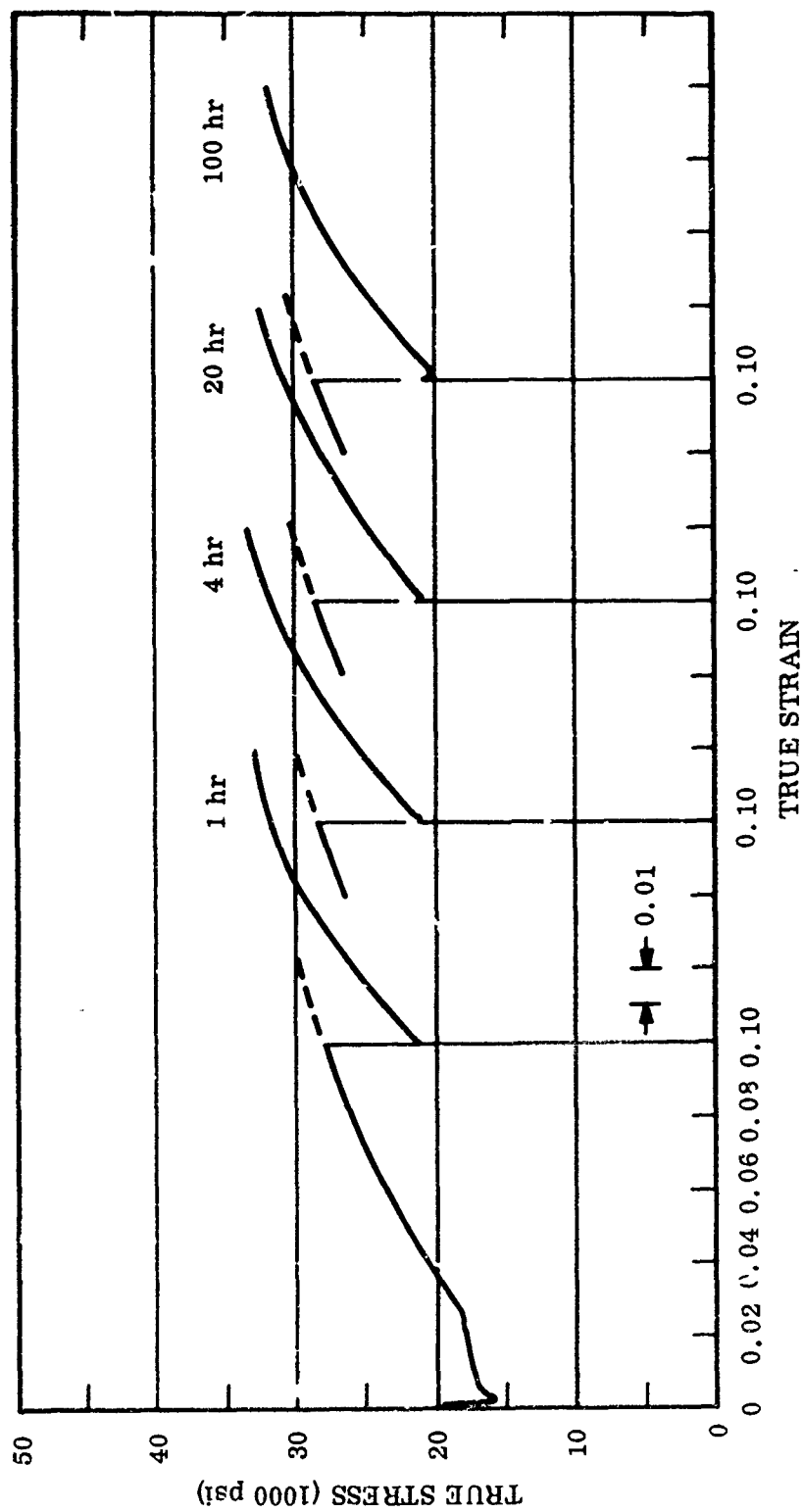
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Fig. 3   Effect of Recovery Treatment at 900°C on the Stress-Strain Behavior of High-Purity Columbium at Room Temperature

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Fig. 3 Effect of Recovery Treatment at 900°C on the Stress–Strain Behavior of High–Purity Columbium at Room Temperature
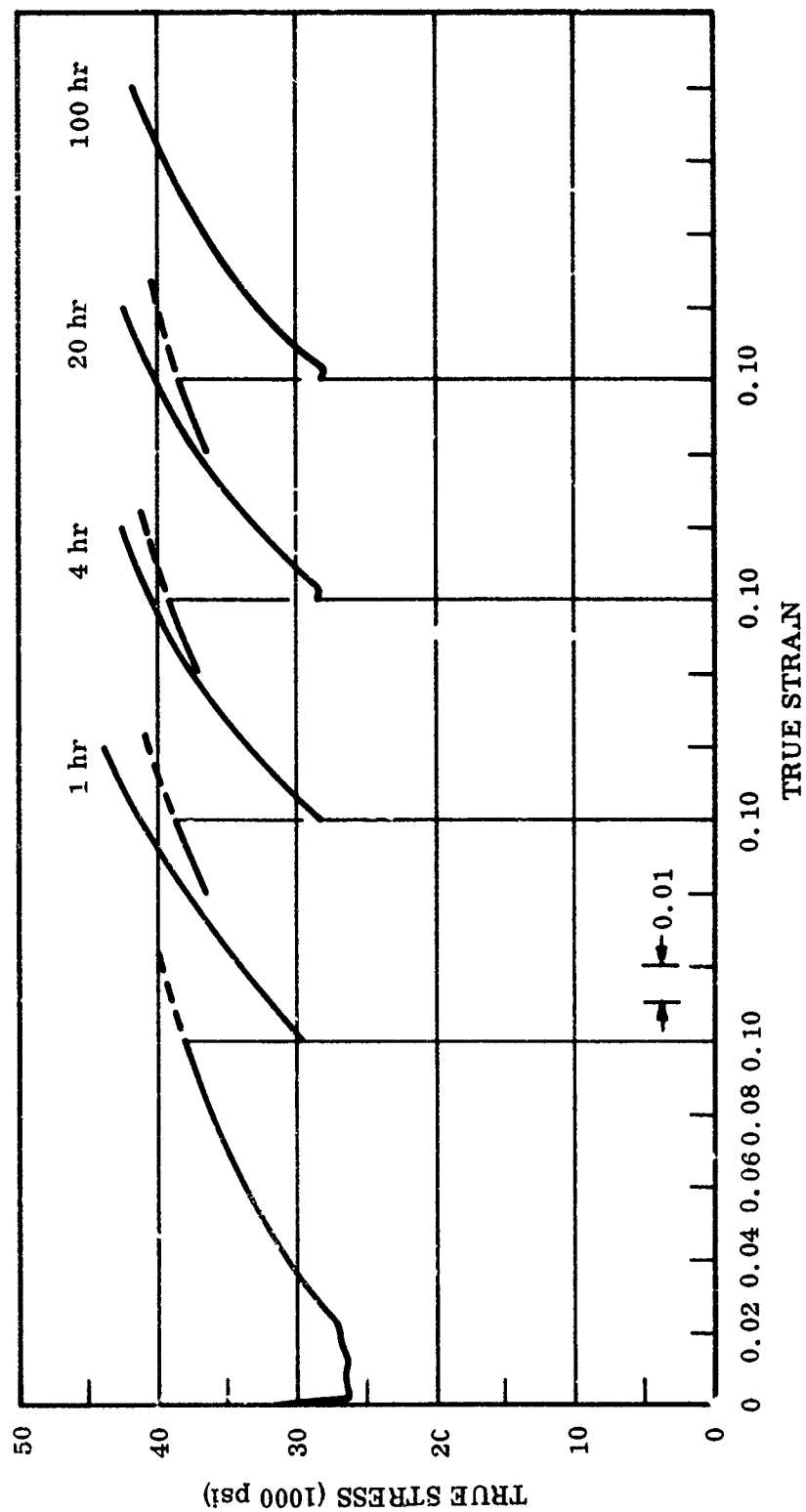
14

Fig. 4 Effect of Recovery Treatment at 900° C on the Stress–Strain Behavior of Cb–1W Alloy at Room Temperature

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Figures 5 and 6 show the fractional flow-stress recovery parameter, f_r, as a
function of recovery time at 800, 900, and 1000°C, for the high-purity columbium and
the Cb-1W alloy, respectively. The recovery behavior of these two materials was
somewhat similar at 800 and 900°C. However, the value of f_r for the Cb-1W alloy
tended to stabilize at the longer recovery times (>20 hr), whereas the flow stress of
the high purity columbium did not stabilize for recovery times up to 100 hr. Also,
the Cb-1W alloy exhibited a greater amount of recovery, in terms of f_r, than did the
high-purity columbium. Thus, the tungsten addition caused an increase in the flow-
stress recovery at these temperatures. The strength levels for the Cb-1W alloys,
however, still exceeded those for the high-purity columbium, as a result of the solid-
solution strengthening effect.

As noted in Fig. 5 , the recovery treatment at 1000°C for 100 hr resulted in re-
crystallization in the unalloyed columbium. This explains the abrupt change in the
f_r versus log time curve for unalloyed columbium at 1000°C. The f_r value of 1.0
indicates the flow stress of the material became equal to that of the as-recrystallized
material. No such break in the f_r versus log time curves or other indication of re-
crystallization occurred in the case of the Cb-1W alloy during exposure at 1000°C.
On the contrary, f_r remained essentially constant during recovery of the Cb-1W
alloy at 1000°C for times between 1 and 100 hr. This effect, as well as the stabiliza-
tion of f_r during exposure at 800 and 900°C, may be attributed to the formation of a
stable dislocation substructure.

The stress-strain curves at room temperature for the Cb-1Zr and Cb-1W-1Zr alloys
recovered for various times at 900°C are illustrated in Figs. 7 and 8 , respectively.
The stress-strain curves of these two alloys are qualitatively very similar. However,
the strength of the Cb-1W-1Zr alloy is considerably greater than that of the Cb-1Zr
alloy for any given value of strain. Although no well-defined yield drop was observed
after recovery at 900°C, inflections in the stress-strain curves were evident in those
specimens recovered for shorter times. The presence of these inflections was also
temperature dependent. They were more prominent after recovery at 800°C and were
essentially absent after recovery at 1000°C. These inflections are thought to be
another manifestation of the oxygen strain-aging phenomenon mentioned earlier. In the

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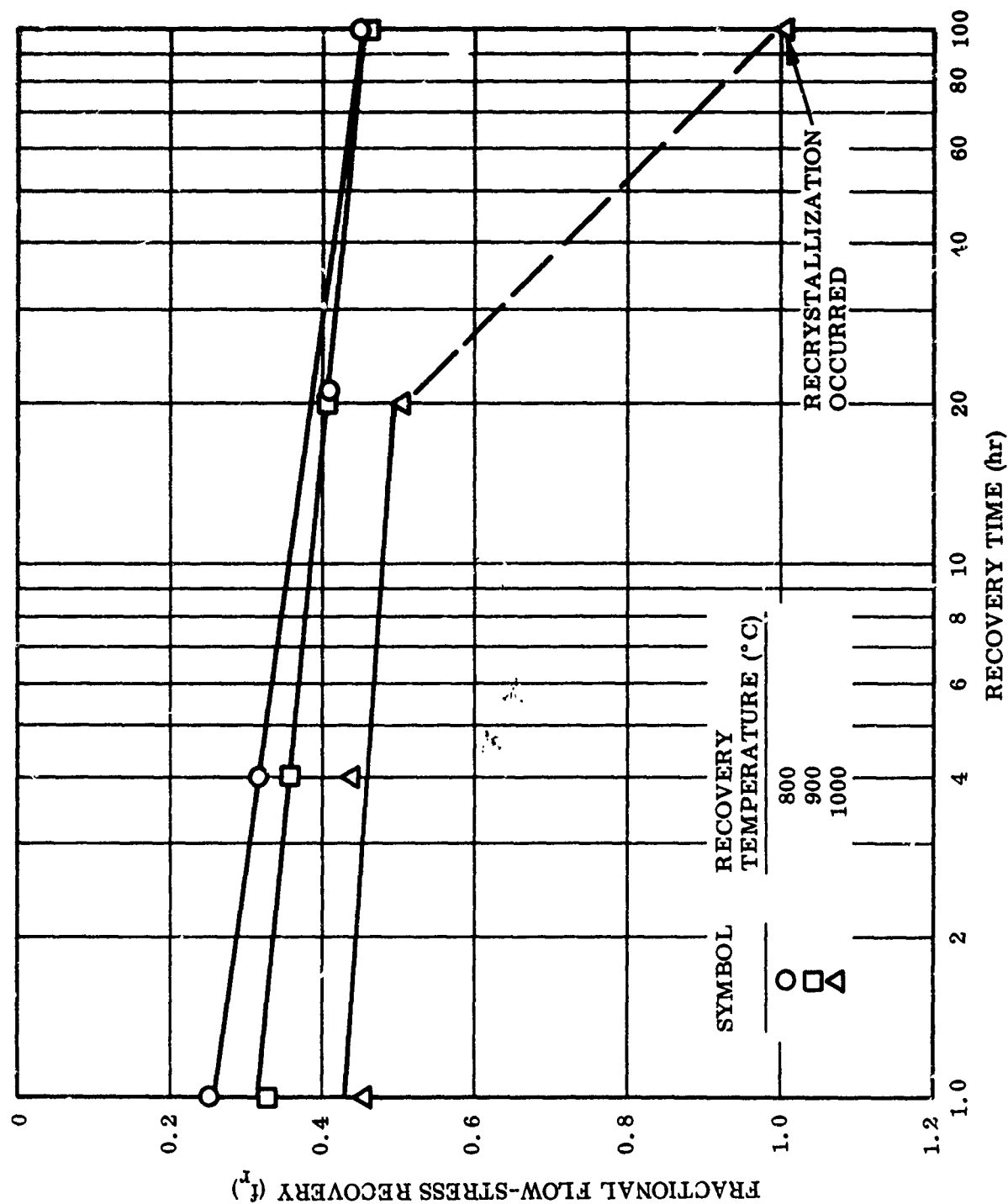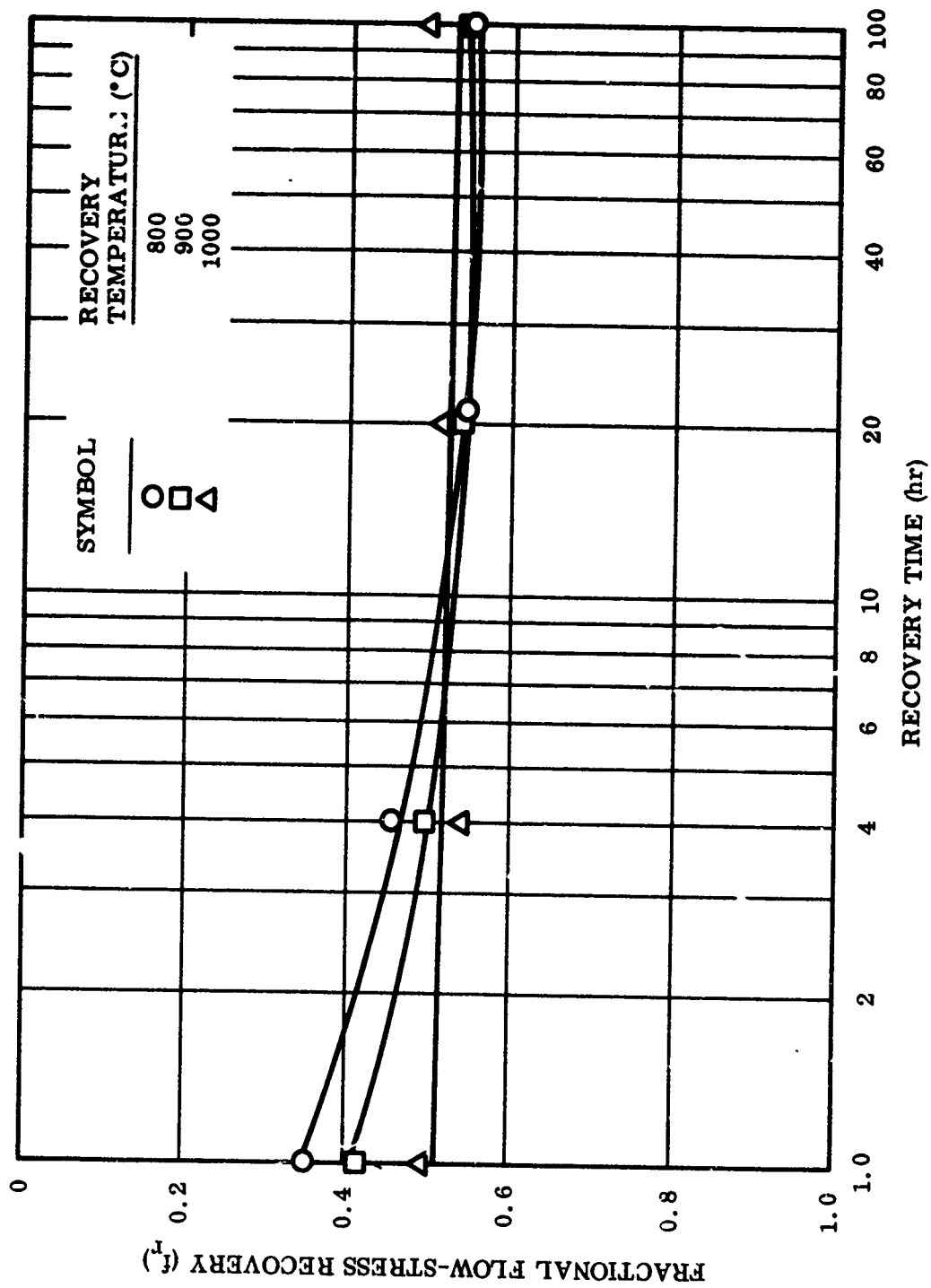Fig. 5   Effect of Recovery Time on the Fractional Flow-Stress Recovery of High-Purity Columbium

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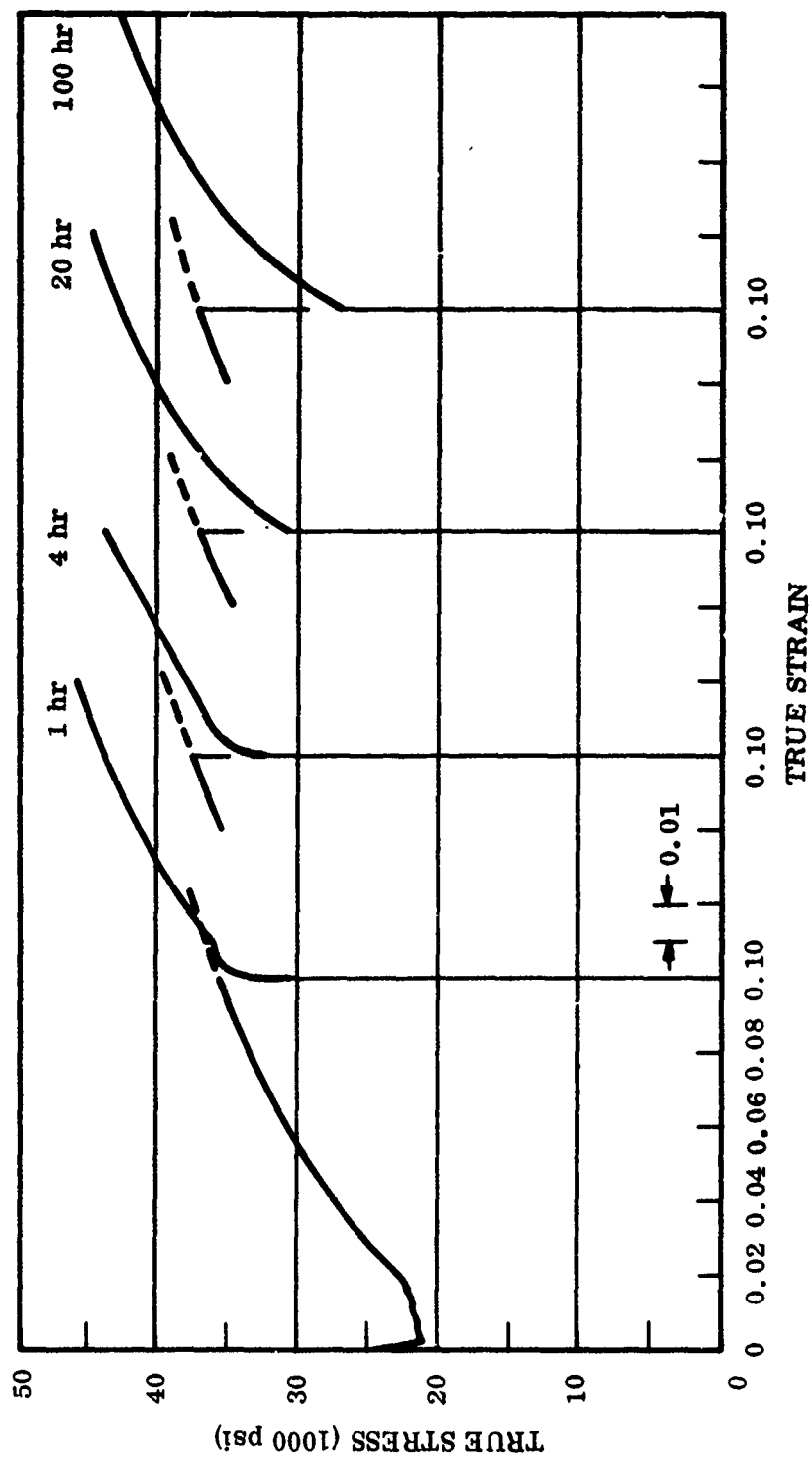Fig. 6   Effect of Recovery Time on the Fractional Flow-Stress Recovery of Cb-1W Alloy

Fig. 7 Effect of Recovery Treatment at 900°C on the Stress-Strain Behavior of Cb-1Zr Alloy at Room Temperature
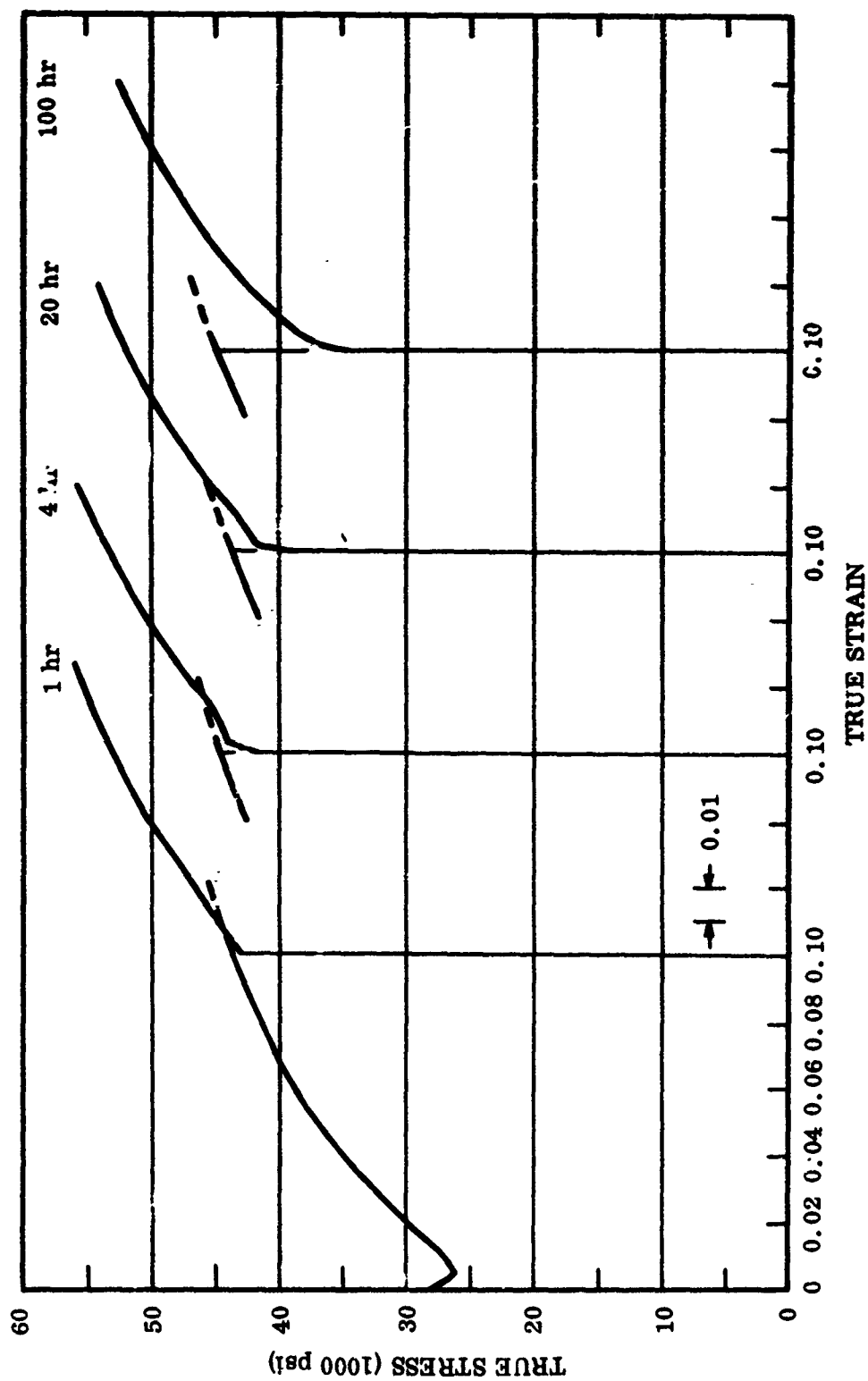
Fig. 8 Effect of Recovery Treatment at 900°C on the Stress-Strain Behavior of Cb-1W-1Zr Alloy at Room Temperature

case of the two alloys containing zirconium, the location of oxygen atoms near dislocation cores would seem to represent a metastable condition. A still lower energy configuration would be achieved when the oxygen atoms associate themselves with zirconium atoms to form zirconium-oxygen rich zones (i.e., coherent precipitates) or actual α-zirconia precipitates. Hence, at higher recovery temperatures or for longer recovery times, the oxygen atoms are thought to diffuse from metastable positions near columbium atoms along dislocations cores to sites adjacent to zirconium atoms also located along the dislocation cores. Electron micrographs, supporting this viewpoint, are presented in section 3.1.3.

Figures 9 and 10 show the fractional flow-stress recovery versus recovery time for the Cb-1Zr and Cb-1W-1Zr alloys, respectively. The recovery behavior of these two alloys in terms of f_r values was almost identical. It is suggested that two competing processes occur which account for the recovery behavior of these alloys: (1) a softening due to annihilation or rearrangement of dislocations, and (2) a hardening effect associated with the formation of zirconium-oxygen precipitates. At 800° C the softening is apparently masked by the hardening effect, with the net result that very little change in f_r is observed. At higher recovery temperatures, softening due to changes in the dislocation configurations occurs more rapidly while effective hardening diminishes since any precipitates that develop are coarser and more widely separated.

3.1.2 Effect of Internal Oxidation on Flow-Stress

Following a 10% tensile prestrain, high-purity columbium, Cb-1W, Cb-1Zr, Cb-1W-1Zr specimens were internally oxidized for times up to 100 hr at 800, 900, and 1000°C. The specimens were then restrained at room temperature.

The stress-strain curves at room temperature of the high-purity columbium and the Cb-1W alloy, receiving various internal oxidation treatments at 900°C, are given in Figs. 11 and 12, respectively. These curves were identical in form to their counterparts shown in Figs. 3 and 4. However, the strengths at any given value

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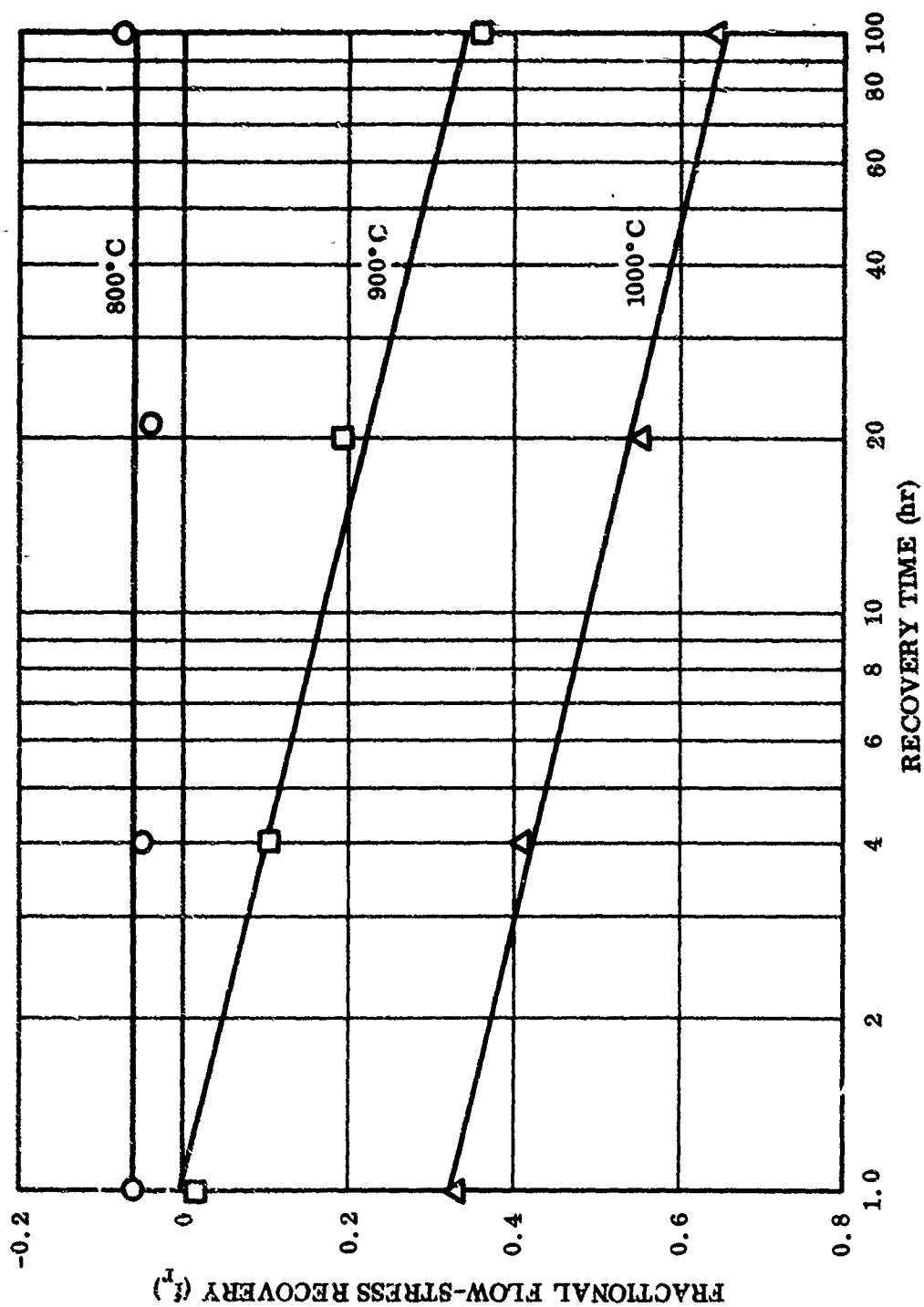
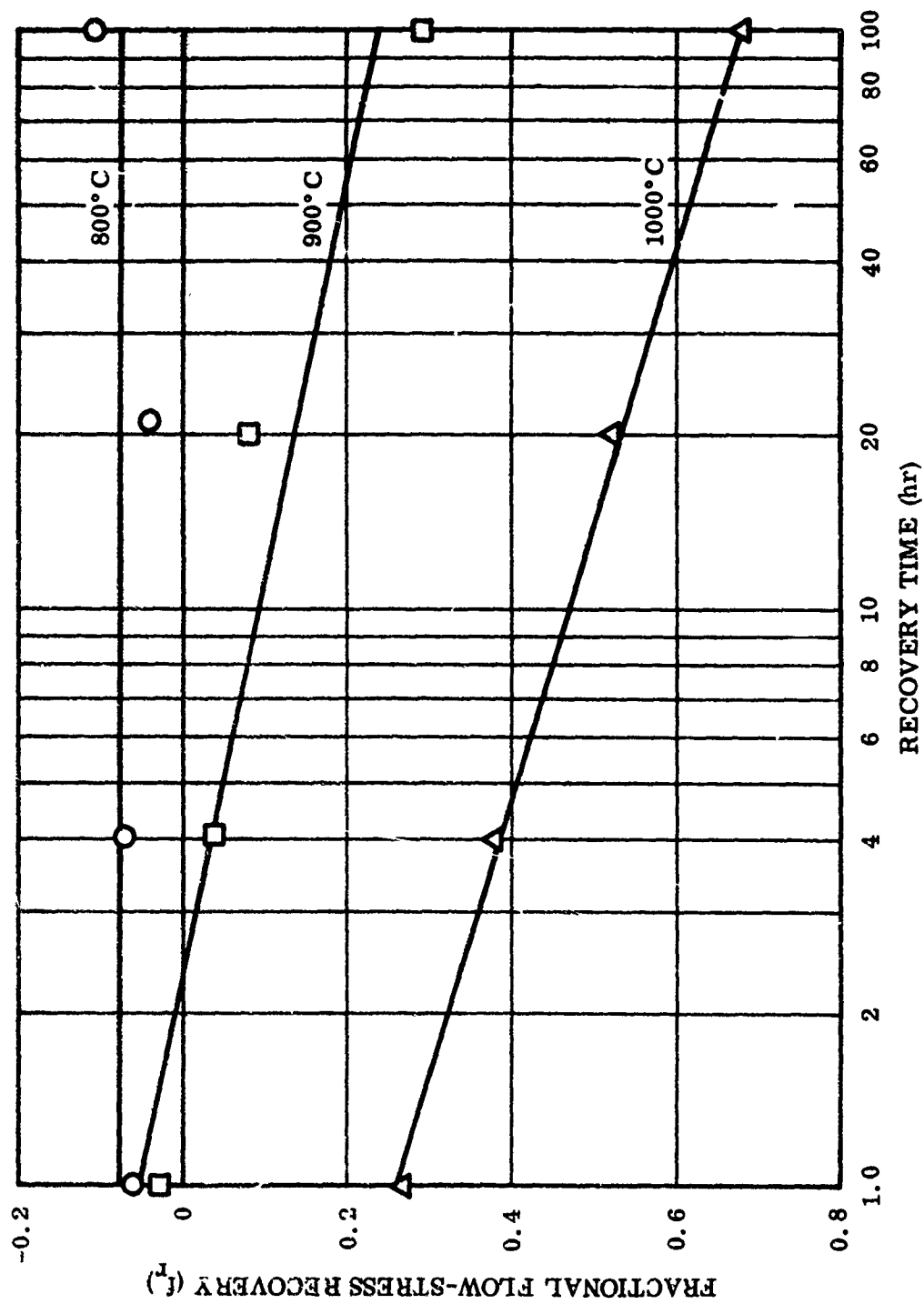Fig. 9 Effect of Recovery Time on the Fractional Flow-Stress Recovery of Cb–1Zr Alloy

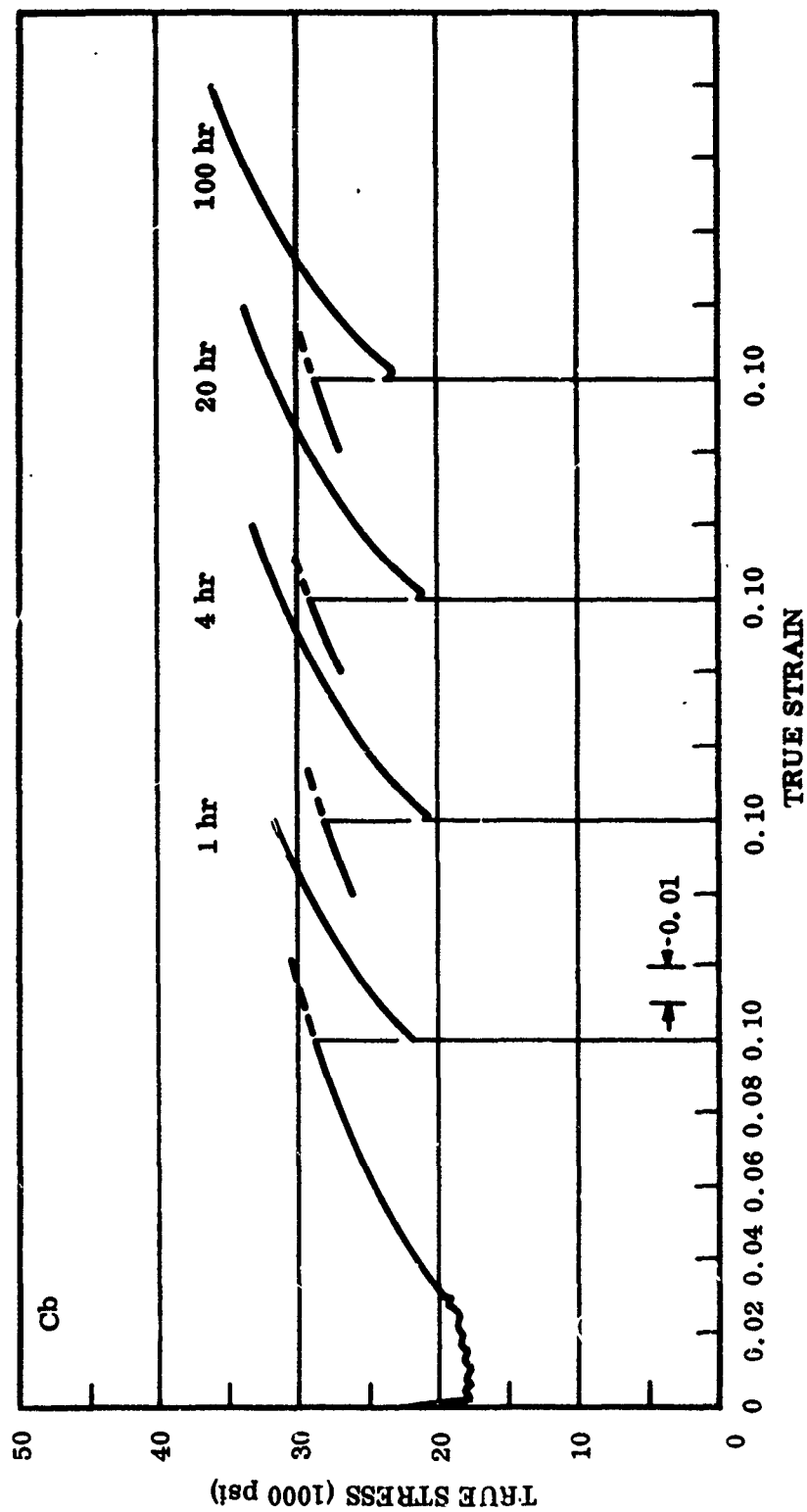Fig. 10 Effect of Recovery Time on the Fractional Flow–Stress Recovery of Cb–1W–1Zr Alloy

23

Fig. 11 Effect of Internal Oxidation Treatment at 900°C on the Stress-Strain Behavior of High-Purity Columbium at Room Temperature
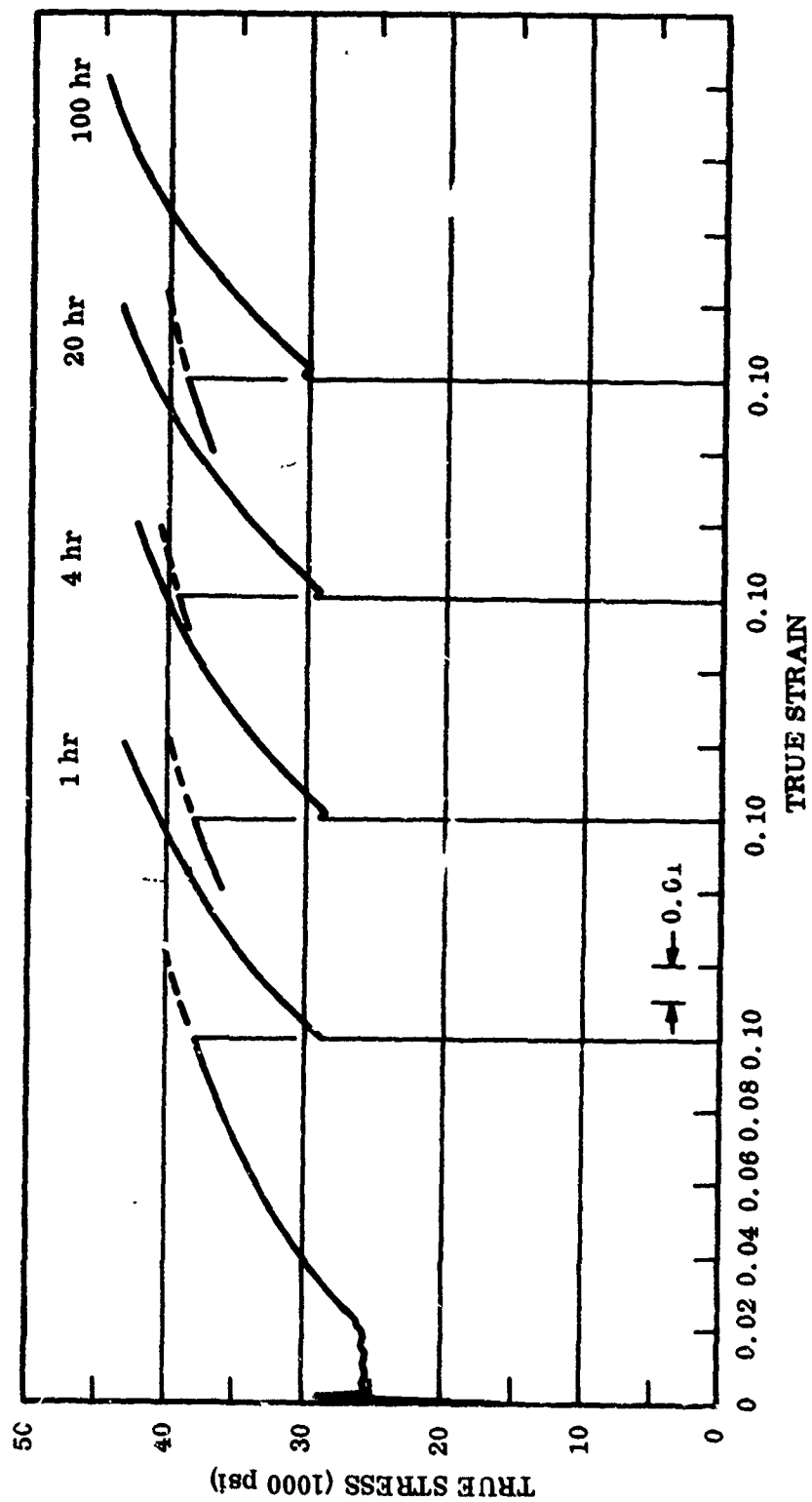
24

Fig. 12 Effect of Internal Oxidation Treatment at 900°C on the Stress-Strain Behavior of Cb-1W at Room Temperature

25

of strain for the high-purity columbium, internally oxidized for 100 hr, and the Cb-1W alloy internally oxidized for 20 or 100 hr, were significantly higher than the strengths developed after recovery. These relative differences in the stress-strain curves were also evident after treatment at 800°C for both materials. After treatments at 1000°C, the relative differences in the strengths for the Cb-1W alloy were smaller than for treatments at 800 and 900°C. These shifts in the stress-strain curves to higher values of stress may be due to oxygen combining with the trace amounts of zirconium in these two materials to form zirconium-oxygen precipitates. The formation of such precipitates produces a strengthening effect. This possible explanation is supported by results discussed in section 3.1.3.

The yield drop and extent of the inhomogeneous strain for the Cb-1W alloy was greater after internal oxidation for 20 and 100 hr than after recovery for corresponding times. This behavior is further evidence that the strain-aging phenomenon is related to the presence of oxygen. The onset of recrystallization prevented any such comparisons being made for the high-purity columbium treated at 1000°C.

The stress-strain curves at room temperature of the Cb-1Zr and Cb-1W-1Zr alloys, receiving various internal oxidation treatments at 800, 900, and 1000°C are summarized in Figs. 13 and 14 , respectively. Both alloys were significantly strengthened by the treatments at 800°C, and the values of flow-stress increased with increasing internal oxidation time. Some strengthening also occurred during internal oxidation of these alloys at 900°C, but the strength levels were considerably lower than those obtained for equivalent times at 800°C. At 1000°C an actual decrease in strength occurred for both alloys.

The longer internal oxidation treatments at 800°C for the alloys containing zirconium resulted in totally different stress-strain behavior than the corresponding recovery treatments at 800°C. The stress-strain behavior, following the internal oxidation treatments at 900°C, more closely approached that exhibited by the alloys recovered at 900°C for equivalent times. The internally oxidized or recovered alloys treated at 1000°C for identical times displayed very similar stress-strain curves. The explanation for this behavior is based on the idea of interaction between oxygen and zirconium atoms.

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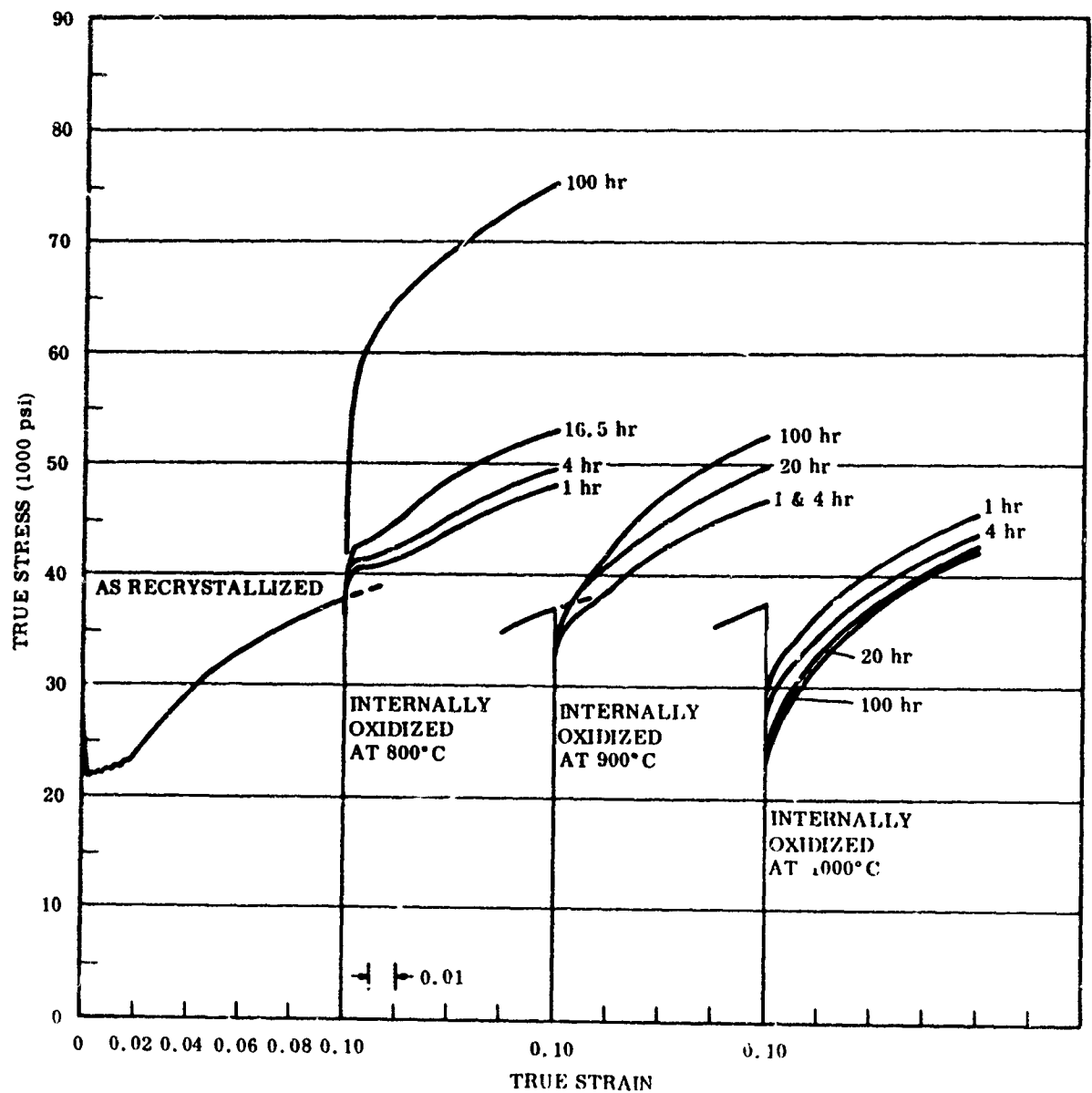
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Fig. 13 Effect of Various Internal Oxidation Treatments on the Room Temperature
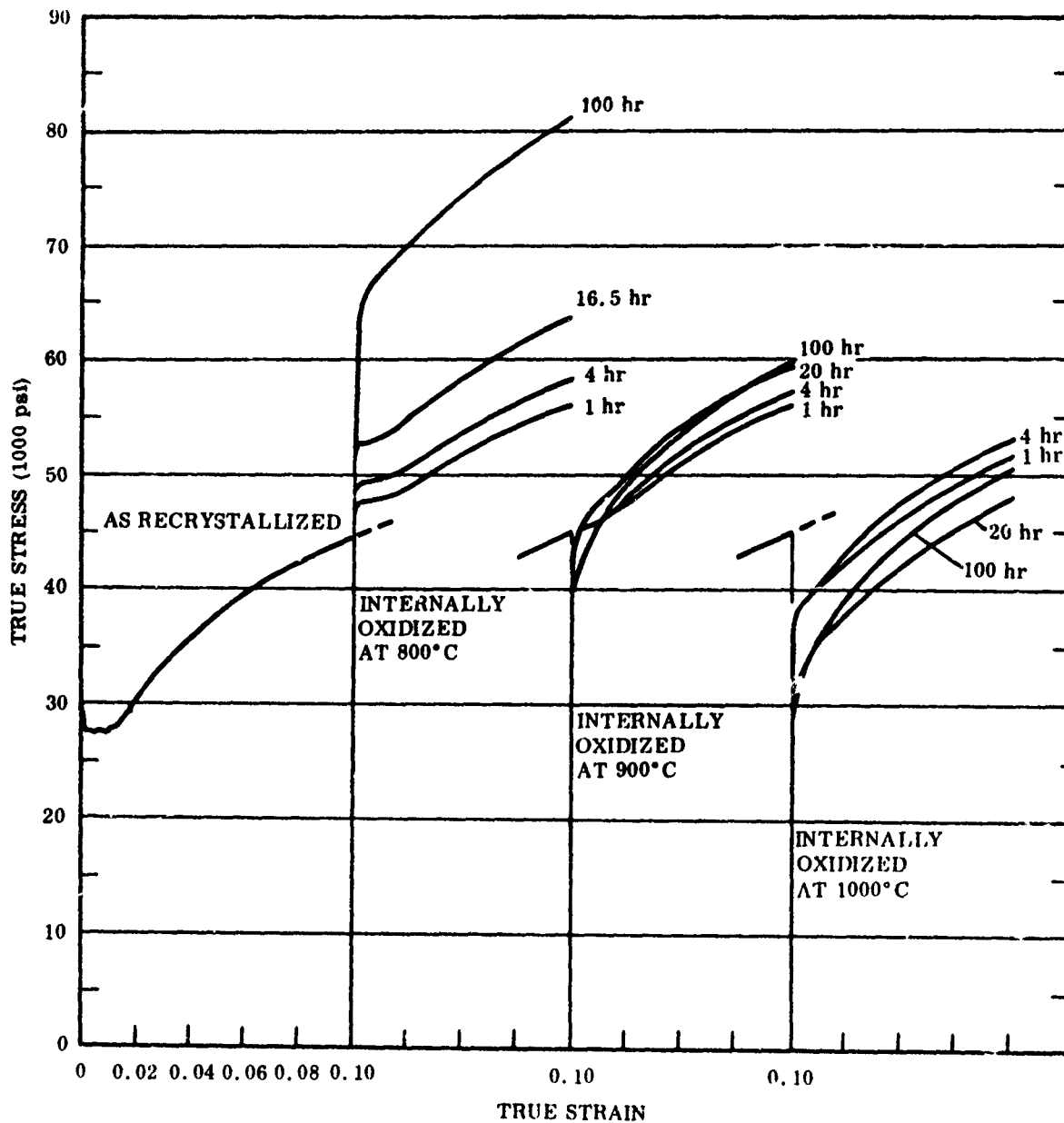Stress-Strain Curves of 10% Prestrained Cb-1Zr Alloy

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Fig. 14 Effect of Various Internal Oxidation Treatments on the Room Temperature Stress-Strain Curves of 10% Prestrained Cb-1W-1Zr Alloy

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3.1.3 Substructures Developed in Cb-1W-1Zr

At room temperature the greatest tensile strengths were developed by the Cb-1W-1Zr
alloy. Thus, this material was chosen for a more detailed study of the structural
changes which occurred during various thermal treatments. After 10% tensile pre-
strain samples of Cb-1W-1Zr were recovered or internally oxidized at 800°C for 1,
20, and 100 hr, and thin foils were taken from the gage sections for electron micro-
scopy. In addition thin foils of the as-prestrained alloy were examined.

Figure 15 shows the sequence of dislocation arrangements produced after straining
and internally oxidizing for times up to 100 hr, while Fig. 16 shows a similar sequence
for the recovery treatments.

As can be seen from these two figures, a cellular substructure has developed in the
alloy after the 10% tensile strain. The cell size is approximately 1 μ and the cell
walls are composed of tangles of dislocations. In many regions the tangles are too
dense for the individual dislocations to be distinguished. However, some relatively
wide, straight dislocations showing strong contrast can be seen in the tangles (e.g.,
at A). These are thought to have remained after recrystallization, due to pinning by
interstitials, and act as barriers which cause the tangles to develop. Dislocations
are noticeably absent from the cell interiors, except for a few loops (e.g., at B).
The dislocation densities seem to be greatest near the loops. This multiplication is
probably accounted for by a double cross slip mechanism involving the screw com-
ponents of loops, such as that suggested by Low and Guard.[9]

The structures developed in this alloy on straining appear to be very similar to those
formed in unalloyed columbium.[3] Van Torne and Thomas[3] suggested that the dis-
location arrangements were closely controlled by the distribution of impurities. They
reported that cellular regions only formed in columbium when precipitates were pre-
sent which acted as effective barriers to glissile dislocations. When the impurities
were all in solid solution, dislocations were observed to be arrayed at random in
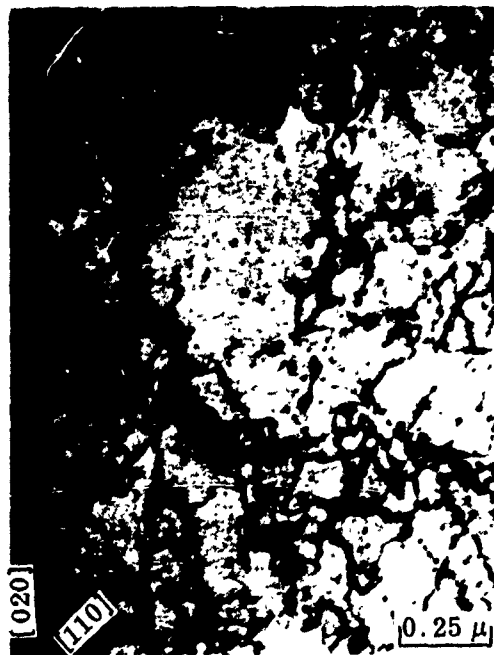each grain for tensile strains up to 22%.

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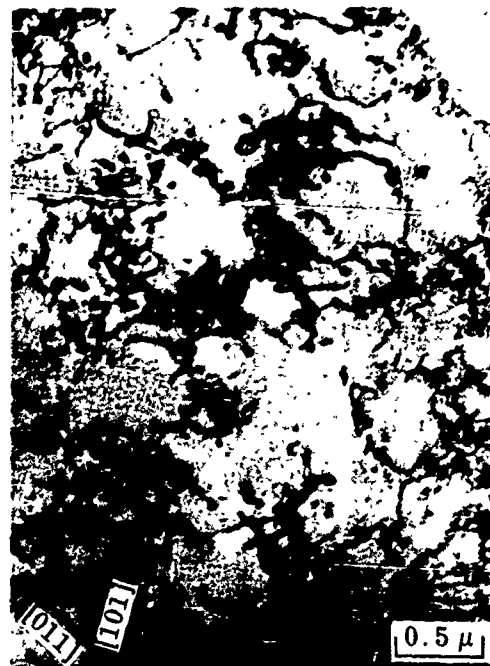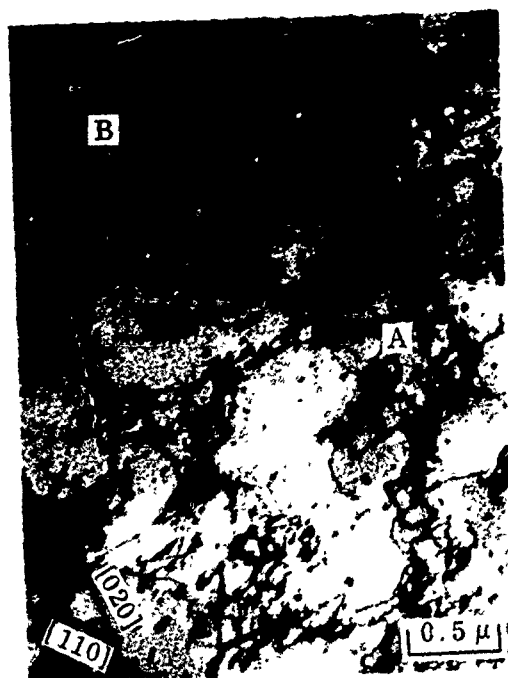
(a) Strained 10%

(b) Annealed 1 hr

(c) Annealed 20 hr

(d) Annealed 100 hr

Fig. 15 Internal Oxidation of Prestrained Cb-1W-1Zr at 800°C

(a) Strained 10%

(b) Annealed 1 hr

(c) Annealed 20 hr

(d) Annealed 100 hr

Fig. 16   Recovery of Prestrained Cb-1W-1Zr at 800°C

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No significant differences could be detected between the substructures developed after recovery or internal oxidation for 1 hr. The cellular structure produced during pre-straining was still evident, but the dislocations in the cell walls were now resolvable.

After 20 hr the cell structure became less evident in the internally oxidized material. However, in one instance considerable dislocation rearrangements were observed, as shown in Fig. 17 . The tangles and loops have largely been eliminated and the dislocations have become aligned at the beginning of network formation. A more representative area of the internally oxidized alloy is shown in Fig. 15 . The apparent widths and image intensities of many dislocations vary along their lengths. This is attributed to clustering of interstitial atoms and the formation of fine precipitates which pinned the dislocations.

In the recovered alloy, little evidence of precipitation was found after 20 hr. As can be seen in Fig. 16 , the cells have largely been eliminated and the dislocation arrangements are much less complex.

After 100 hr many small precipitates were observed on the dislocations in the internally oxidized alloy as shown in Fig. 15 . The dislocations appeared in very high contrast compared with those in the recovered alloy (Fig. 16), which is a further indication of clustering of interstitial atoms. No regular dislocation arrays were seen for the alloy in this condition, but the cellular pattern typical of the as-prestrained alloy was largely eliminated.

Following recovery for 100 hr, rearrangement of dislocations into more stable, regular configurations occurred in some areas, as shown in Fig. 16 . However in other grains cell structures in various stages of rearrangement were still to be found, as shown in Fig. 18 . These variations are not altogether unexpected, since the amount of strain in each grain depends upon its orientation with respect to neighboring grains and to the tensile axis.
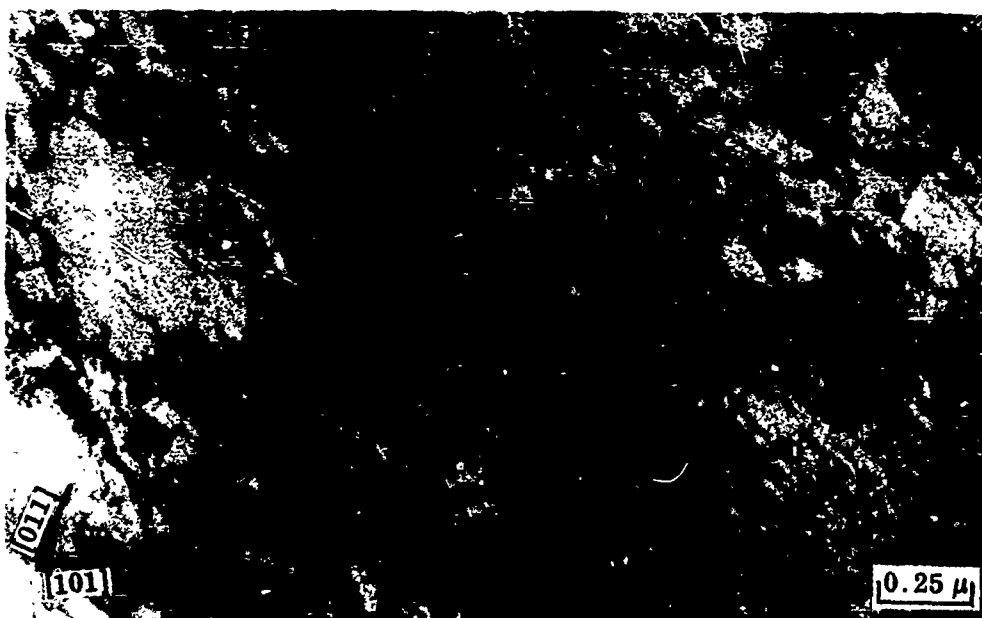
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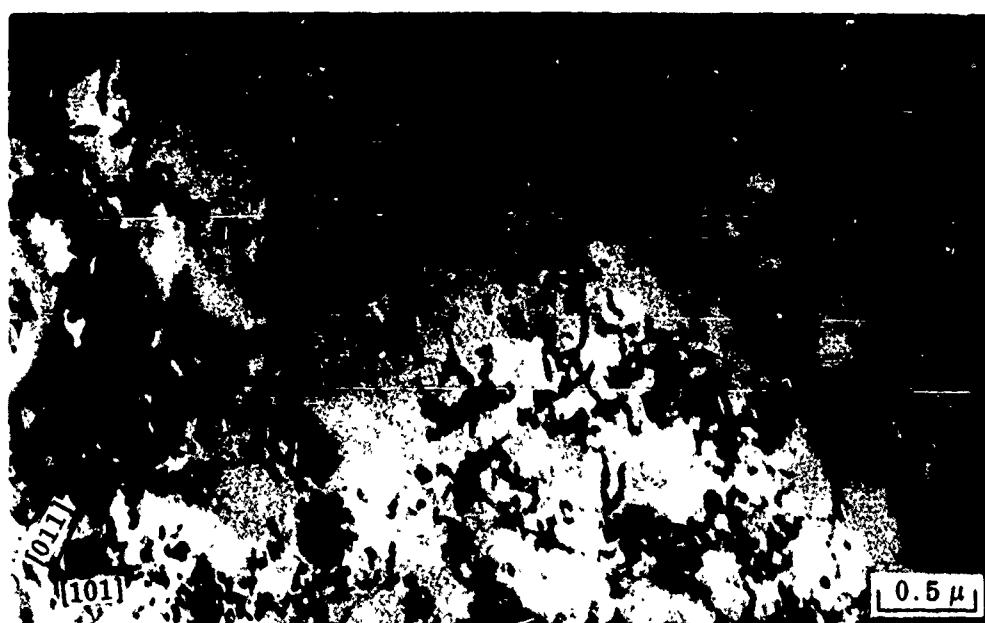Fig. 17   Cb-1W-1Zr Prestrained 10% and Internally Oxidized for 20 hr at 800°C

Fig. 18   Cb-1W-1Zr Prestrained 10% and Recovered for 100 hr at 800°C

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3.2 INTERNAL OXIDATION OF RECRYSTALLIZED Cb-1W-1Zr

3.2.1 Mechanical Properties at Room Temperature

In an effort to obtain a better understanding of the effects of internal oxidation treatments on the mechanical properties of the Cb-1W-1Zr alloy, several specimens in the as-recrystallized condition were internally oxidized at 800°C for 16.5 and 100 hr. Figure 19 illustrates the true stress – true strain curves obtained for the alloy after these two treatments.

A number of points concerning the stress-strain curves of Fig. 19 are of interest. Firstly, the magnitude of the flow stress increased as the internal oxidation treatment time increased. After the 100-hr treatment, both the flow-stress and the ultimate tensile stress were approximately twice those of the as-recrystallized alloy. Some variation was noted between the strengths achieved by specimens internally oxidized in different batches, though the strengths of specimens in the same batch were very similar. These differences were attributed to small changes in the operating pressure of the vacuum annealing furnace. Secondly, the yield drop present in the as-recrystallized alloy was eliminated by the internal oxidation treatments. This phenomenon and the elimination of the inflections in the stress-strain curves of the prestrained-recovered or prestrained-internally oxidized Cb-1Zr and Cb-1W-1Zr alloys (section 3.1.1) are thought to occur by the same mechanism. Lastly, the strain hardening rate of the alloy was unchanged by the internal oxidation treatment. This latter point suggests that the precipitates formed during internal oxidation at 800°C are zones coherent with the matrix, since the rate of strain hardening of an alloy containing zones is virtually the same as that of zone-free material. In alloys containing non-coherent precipitates the rates of strain hardening are generally very high, since dislocations cannot shear the particles but are forced between them.[10]

3.2.2 Zone Formation and Stability

To study the strengthening effect more fully, thin foils were made from the recrystallized Cb-1W-1Zr alloy which had been internally oxidized at 800°C for 100 hr. Transmission
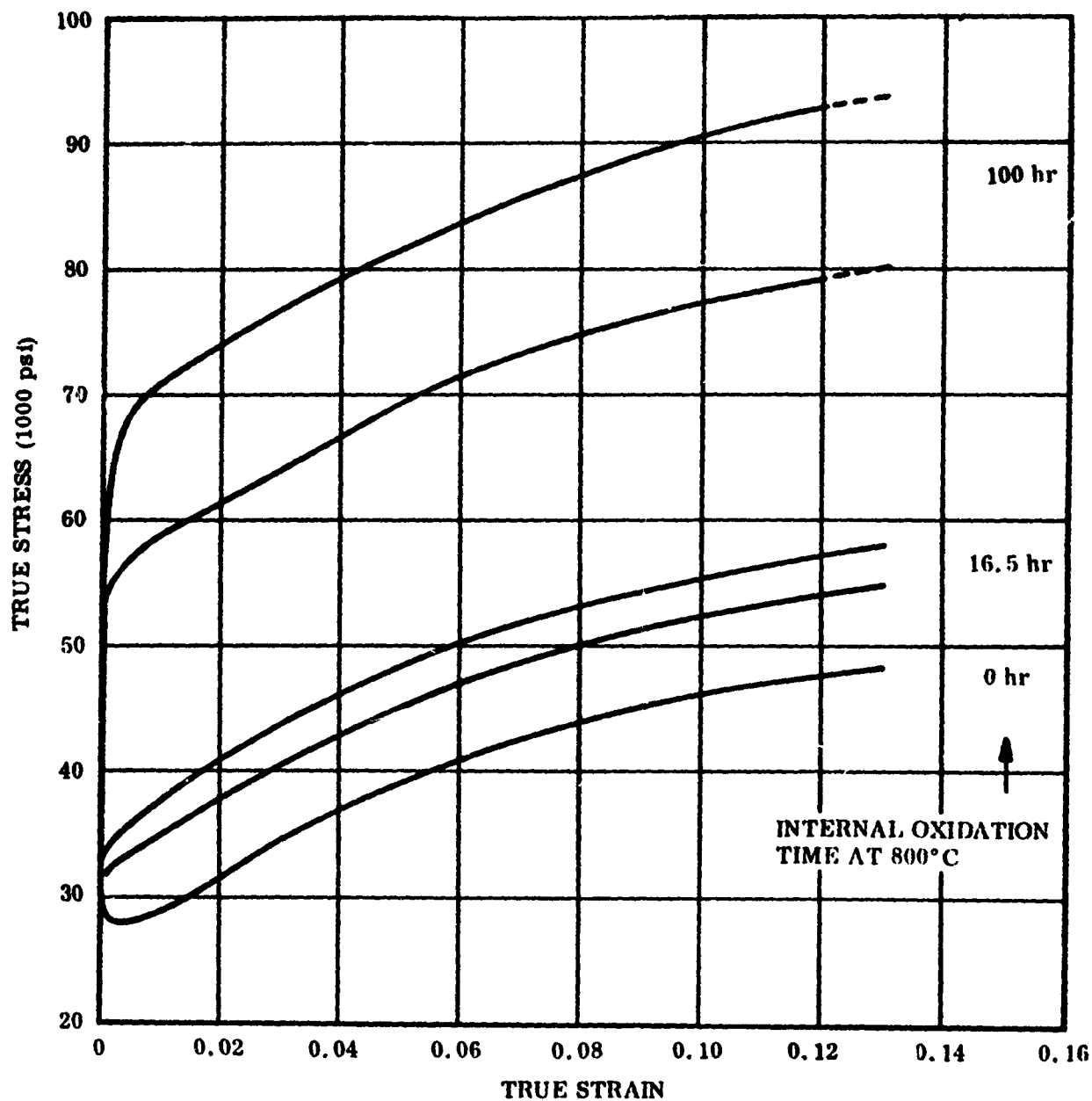
34

Fig. 19 Effect of Internal Oxidation at 800°C on the Stress-Strain Behavior of
Cb-1W-1Zr Alloy at Room Temperature

electron microscopy revealed an extremely high density of precipitates less than
100 Å in size. Examples are shown in Fig. 20.

The precipitate images appear as black-white regions divided by a line of no contrast.
These are strain contrast images;[11-13] they indicate that there is an elastic strain
field associated with each particle, suggesting that the particles are in fact zones
coherent with the matrix. Other evidence supporting this view is that the rates of
work hardening of the as-recrystallized and the internally oxidized materials are
almost identical[10] (see Fig. 19) and also that no extra diffraction spots could be
detected from areas containing these fine precipitates. However, a few, isolated
precipitates up to $0.5~\mu$ were found which gave extra reflections. An example is
shown in Fig. 21 . The selected area diffraction pattern was taken over the largest
precipitate in the center of the field. The precipitate was identified as monoclinic
zirconium oxide (ZrO_2). There is a coincidence of ($\bar{1}10$) matrix and ($1\bar{2}0$) precipitate
spots indicating that this precipitate is still partially coherent with the matrix.

An extensive dark field electron microscope investigation would be required to deter-
mine morphological details of the zones and the magnitude and shape of the strain
fields. However, since the particle size and distribution is considered the major
factor influencing the mechanical properties of the material, a study of the thermal
stability of the zones was thought to be of greater value at this time. Consequently,
thin foils were prepared from the Cb-1W-1Zr alloy after internal oxidation at 900°C
for 100 hr. Typical electron micrographs are shown in Fig. 22 . Coherent particles
were still produced at this higher temperature, but they are considerably larger with
a greater interparticle spacing. In some areas of the micrographs double-arc,
strain-contrast images with a well-defined line of no contrast can be seen (e.g., at
A in Fig. 22).

The alloy containing zones produced at 800°C was annealed at 1100°C for 1 hr and thin
foils prepared. Whereas the nucleation of zones at 800 and 900°C seemed to be random
(e.g., Figs. 20 and 22), after 1 hr at 1100°C, the zones appear to have dissolved

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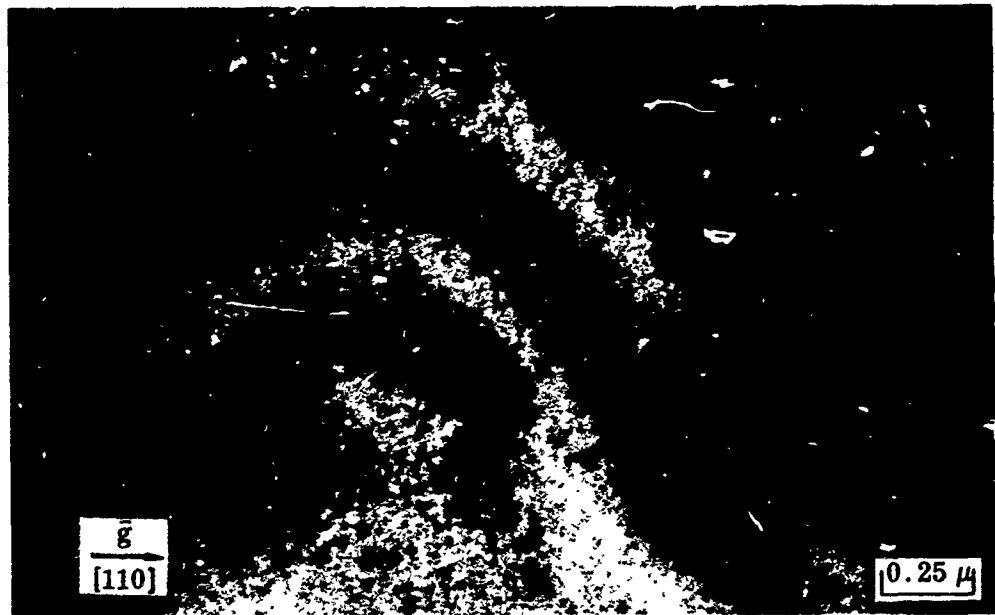
(a) Strain Contrast Images of Zirconium-Oxygen Zones
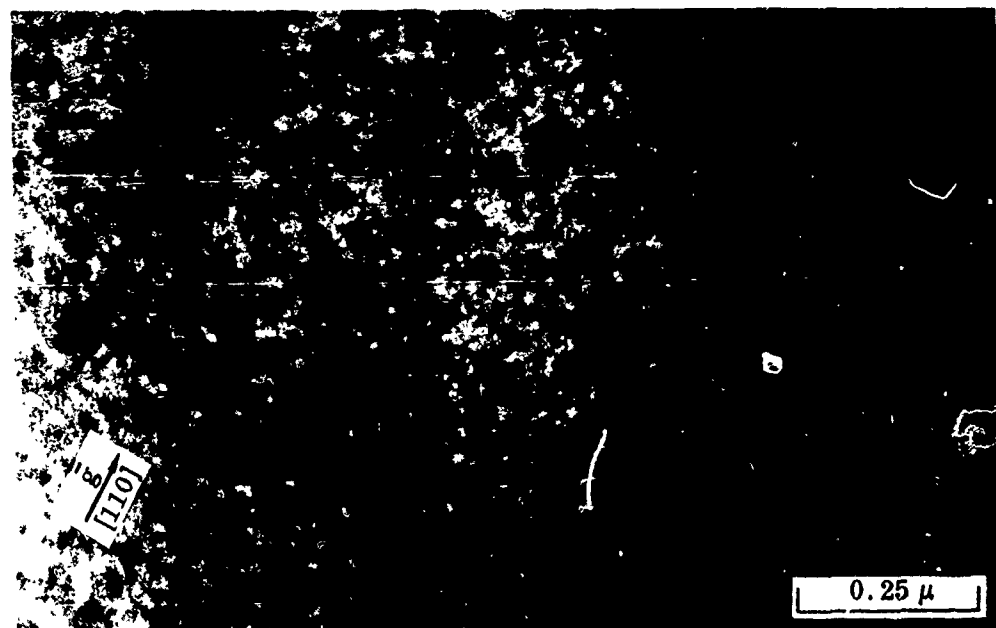
(b) Strain Contrast Images of Zirconium-Oxygen Zones

Fig. 20   Cb-1W-1Zr Internally Oxidized for 100 hr at 800°C

(a) Large Precipitate of Zirconium Oxide

(b) Selected Area Diffraction Pattern Taken Over the Large Precipitate in (a)
[Note $(1\bar{1}0)$ matrix is coincident with $(\bar{1}20)$ precipitate]

Fig. 21 Cb-1W-1Zr Internally Oxidized for 100 hr at 800°C

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(a) Large Precipitate of Zirconium Oxide

(b) Selected Area Diffraction Pattern Taken Over the Large Precipitate in (a)
[Note $(1\bar{1}0)$ matrix is coincident with $(\bar{1}20)$ precipitate]

Fig. 21 Cb-1W-1Zr Internally Oxidized for 100 hr at 800°C

(a) Homogeneous Nucleation of Zirconium-Oxygen Zones

(b) Double Arc Strain Contrast Images (e.g., at A)

Fig. 22 Cb-1.-1Zr Internally Oxidized 100 hr at 900°C

and reformed preferentially at the grain boundaries. Examples are shown in Fig. 23.
It was found that internal oxidation at 1000°C for 20 hr also produced preferential
precipitation at the grain boundaries, but in this case the precipitates were much
larger.

3.3 CREEP BEHAVIOR OF Cb-1W-1Zr ALLOY

As noted earlier, the internal oxidation treatment at 800°C for 100 hr resulted in a
two-fold increase in the yield and ultimate tensile strengths of the Cb-1W-1Zr alloy
at room temperature. A point of greater interest. however, is the effect of internal
oxidation on the mechanical properties at elevated temperatures. Thus, creep-rupture
tests were performed at 1200°C at two values of stress: 9000 and 13,000 psi. The
structural changes occurring during creep were studied by transmission microscopy
and are also reported in this section.

3.3.1 Creep Rupture Tests

Five alloy conditions were selected for investigation. These conditions were (1) as-
recrystallized, (2) prestrained 10%, (3) internally oxidized, (4) prestrained-recovered,
and (5) prestrained-internally oxidized. All recovery and internal oxidation treatments
were at 800°C for 100 hr. The latter two conditions were selected for major emphasis
to establish the relative effectiveness of the recovery and internal oxidation treatments
as strengthening mechanisms at elevated temperatures.

Creep curves for the Cb-1W-1Zr alloy at 1200°C, in each of the five conditions, are
presented in Fig. 24 for 9000 psi and in Fig. 25 for 13,000 psi. At both stress
levels, the internal oxidation treatment resulted in a substantial improvement in the
creep resistance. The creep data are summarized for all five material conditions in
terms of rupture time and time to 0.05 strain in Table 1 , and in terms of stress
versus rupture time in Fig. 26 . The maximum difference in rupture life was
observed at the higher creep stress level between the as-recrystallized and the
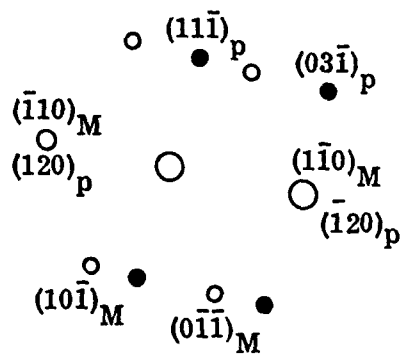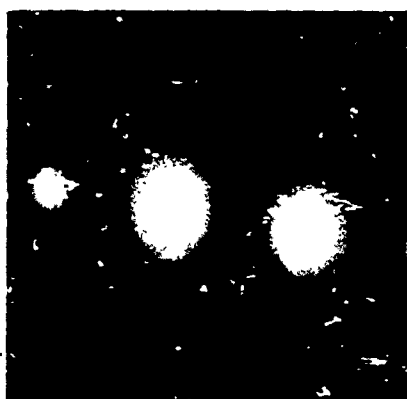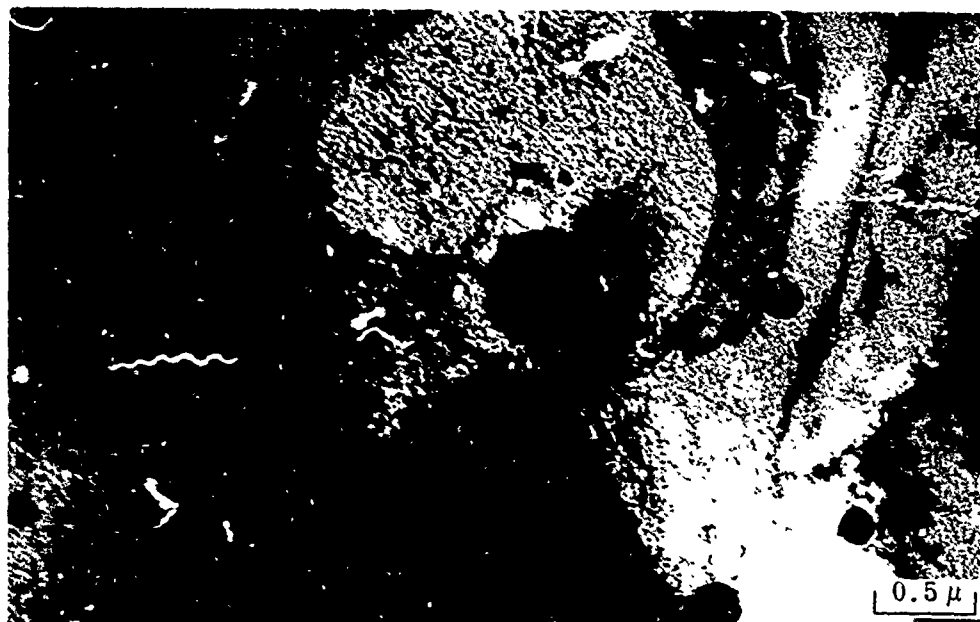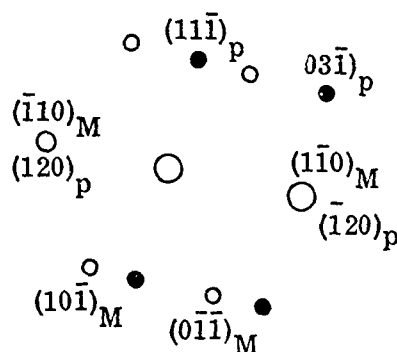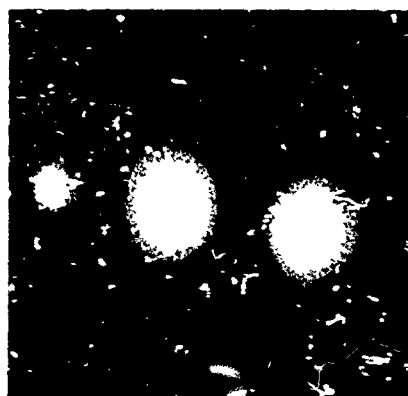
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(a) Preferential Grain Boundary Precipitation
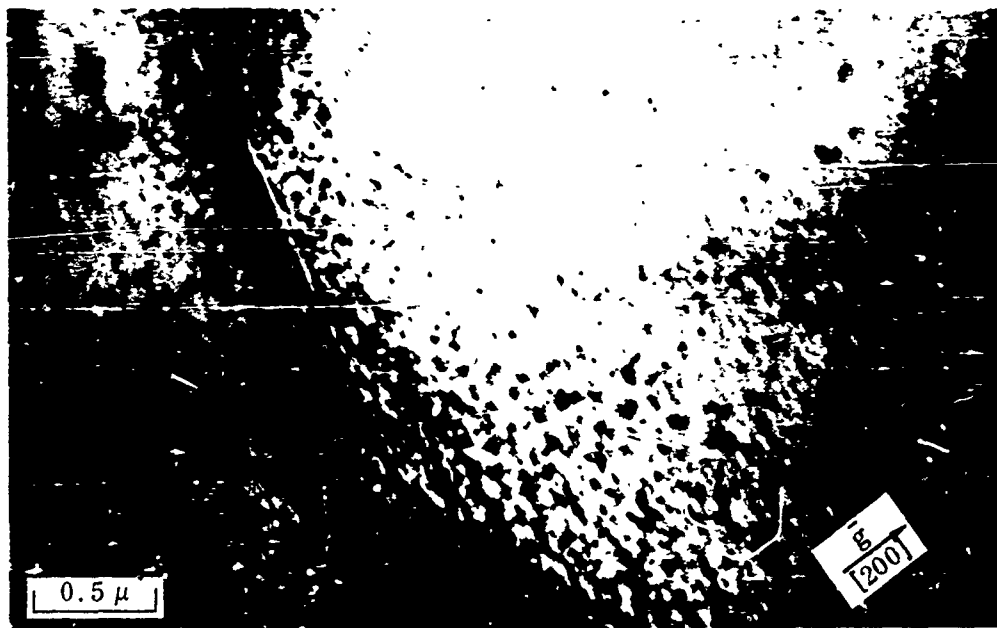
(b) Strain Contrast Images of Zirconium-Oxygen Zones

Fig. 23 Cb-1W-1Zr Internally Oxidized for 100 hr at 800°C. Then Annealed for 1 hr at 1100°C

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Fig. 24 Creep Curves for Cb-1W-1Zr Alloy at 1200°C (2200°F) and 9000 psi

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Fig. 25 Creep Curves for Cb-1W-1Zr Alloy at 1200°C (2200°F) and 13,000 psi

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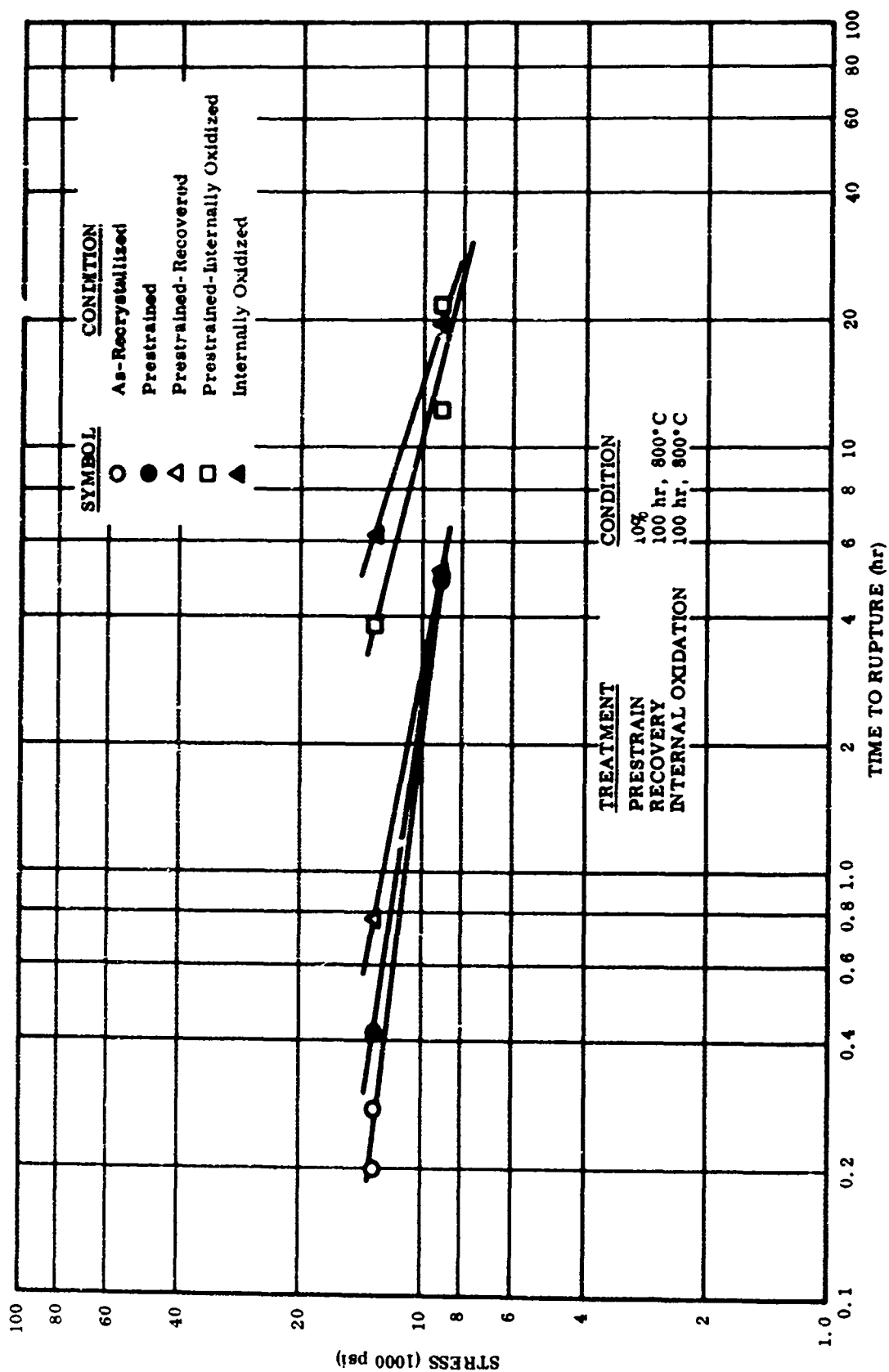
Fig. 26 Stress Versus Time to Rupture for Cb-1W-1Zr Alloy at 1200°C (2200°F)

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Table 4

CREEP DATA FOR THE Cb-1W-1Zr ALLOY TESTED AT 1200°C (2200°F) IN VACUUM

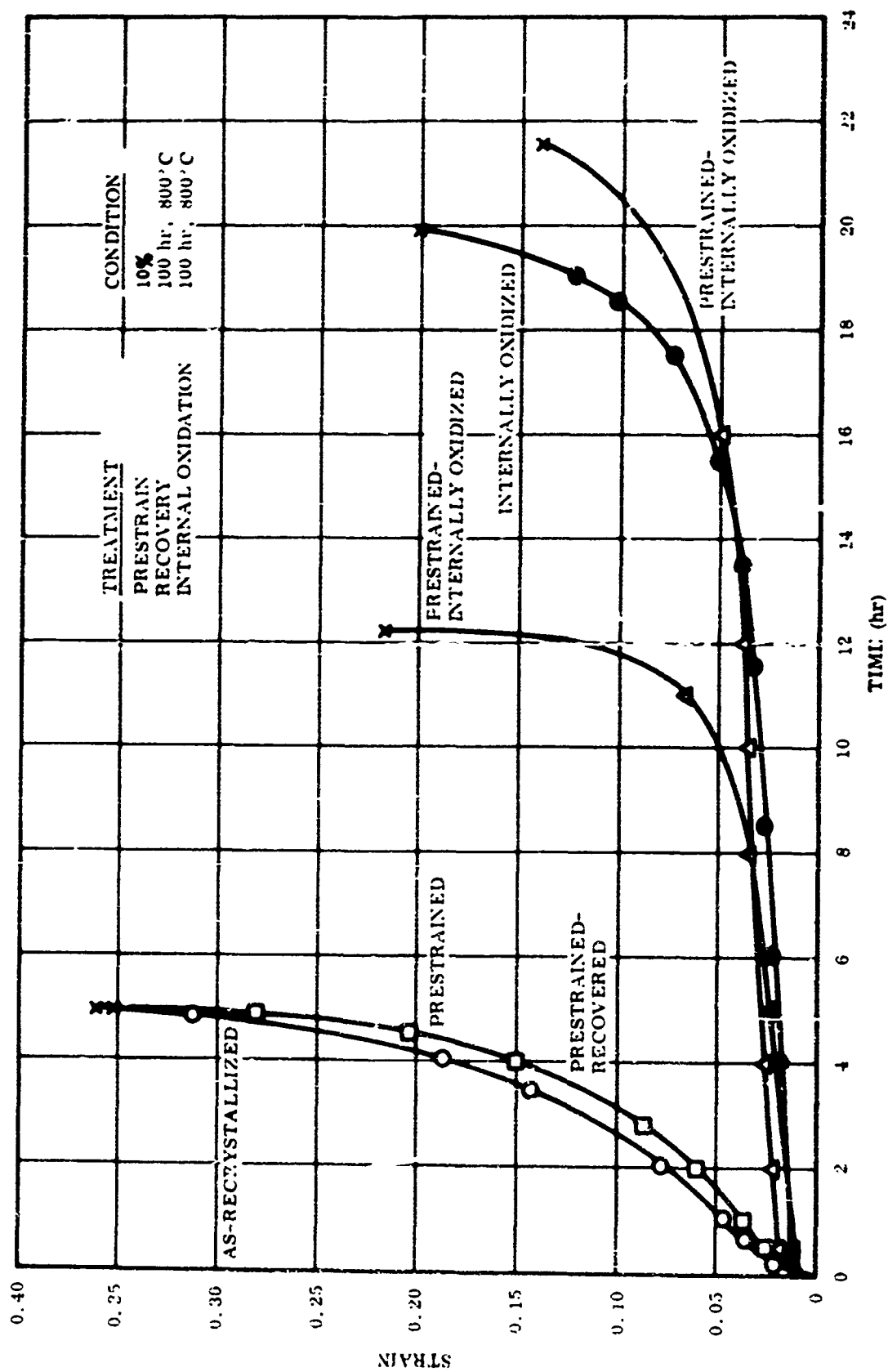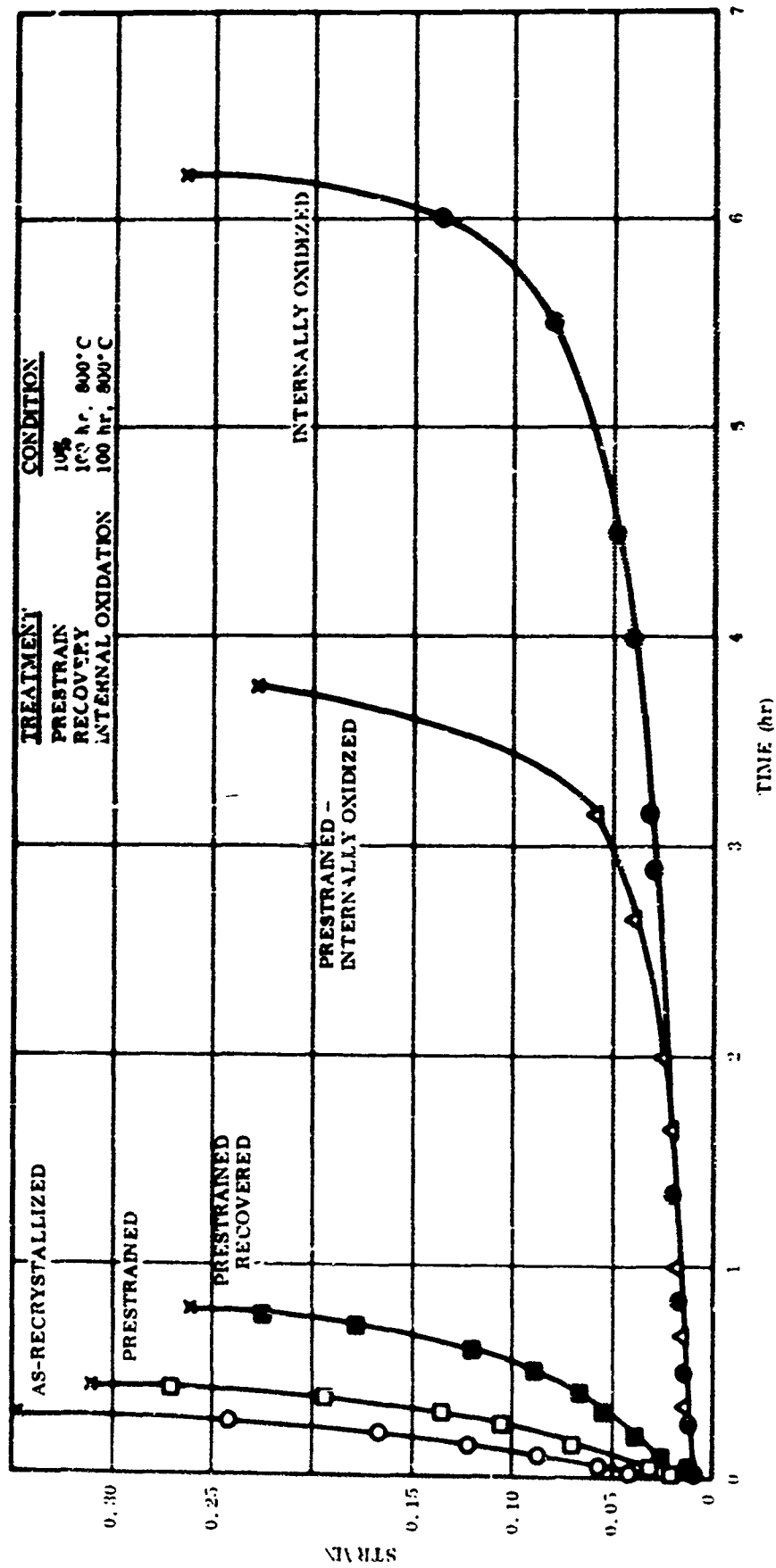| Alloy Condition[a]	9000 psi		13,000 psi	
	Time to 0.05 Strain (hr)	Time to Rupture (hr)	Time to 0 05 Strain (hr)	Time to Rupture (hr)
As-Recrystallized	1.2	4.9	0.04	0.27
Prestrained	1.6	4.9	0.10	0.36
Prestrained-Recovered	1.6	4.9	0.28	0.77
Internally Oxidized	15.4	19.9	4.56	6.2
Prestrained-Internally Oxidized	10.1 16.3	12.2 21.5	2.98	3.76

(a) All prestrain treatments were 10% true strain and all recovery treatments and internal oxidation treatments were for 100 hr at 800°C.

internally oxidized conditions. In this case more than a twenty fold increase in the stress rupture life was observed. From an engineering standpoint, a more meaningful criterion is the time required to achieve some allowable value of total strain. Such comparisons can be made by reference to Figs. 24 and 25 for various values of strain, or by reference to Table 4 for a selected value of strain of 0.05. On the basis of time to 0.05 strain at 13,000 psi, the alloy in the internally oxidized condition was more than a hundred times as creep resistant as in the as-recrystallized condition.

Additional comments of interest can be made with reference to the creep data presented in Table 4 . At a creep stress of 13,000 psi, the prestrained alloy was somewhat more creep resistant than the as-recrystallized alloy as measured by the time to 0.05 strain. On the same basis the prestrain-recovery treatment resulted in about a seven-fold increase in creep resistance over that of the as-recrystallized alloy. However, for the test results at the lower stress level of 9000 psi, the difference

between these three conditions is practically nil. Both the prestrained and the prestrained-recovered conditions initially showed a slight superiority over the as-recrystallized condition, as illustrated in Fig. 24 , but after about 3 hr at 1200°C all three conditions exhibited about equal creep rates and all had equal rupture times of 4.9 hr. The creep properties of the alloy in the internally oxidized condition and in the prestrained-internally oxidized condition are closely comparable.

These observations suggest that at 1200°C the strengthening effect due to the presence of dislocations is retained only for short times; however, it is noteworthy that the structures developed after prestraining and recovery are more creep resistant than those produced by prestraining alone. For longer times the main strengthening effect appears to be a result of the internal oxidation treatment only.

3.3.2 Substructural Changes During Creep

Changes in the substructure occurring during creep of the Cb-1W-1Zr alloys were studied for the material in two initial conditions: (1) prestrained-recovered for 100 hr at 800°C, and (2) prestrained-internally oxidized for 100 hr at 800°C. Creep tests were conducted at 1200°C at a stress of 9000 psi. The creep tests were interrupted (that is, the tests were terminated for foil preparation) at values of total strain of 2% and 9%. These strain values represented steady state and tertiary creep conditions, respectively.

After 2% creep strain at 1200°C. dislocation networks were readily observed in the recovered alloy, but were less evident in the internally oxidized material. Typical micrographs are shown in Figs. 27 and 28 . Dislocations in the internally oxidized material appeared to be associated with precipitates which were occasionally very large (e.g., at A in Fig. 28). Pinning of the dislocations by precipitates apparently hindered rearrangement and subsequent network formation. The exposure time at 1200°C to reach 2% strain was only 1.2 hr for the alloy in the recovered condition, whereas it was 5.5 hr in the internally oxidized condition. During the creep tests,

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(a) Well–Developed Dislocation Network
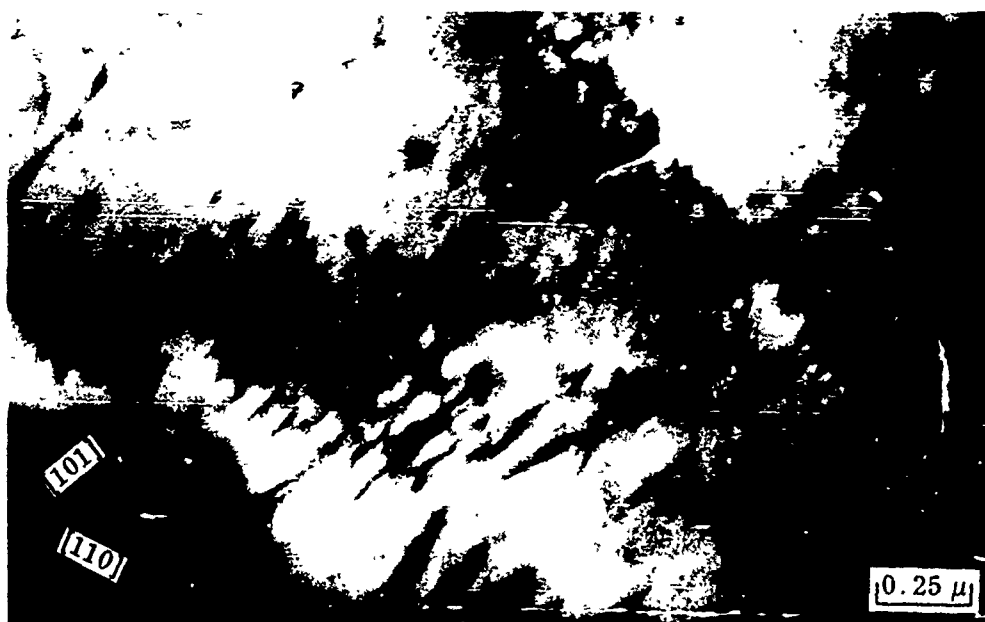
(b) Small Dislocation Network

Fig. 27   Cb-1W-1Zr Prestrained-Recovered for 100 hr at 800°C Then
Creep Tested to 2% Strain at 1200°C

(a) Precipitates Along Dislocations

(b) Large Precipitates, Probably Zirconium Oxide, and Dislocations in Early Stages of Network Formation

Fig. 28 Cb-1W-1Zr Prestrained-Internally Oxidized for 100 hr Then Creep Tested to 2% Strain at 1200°C
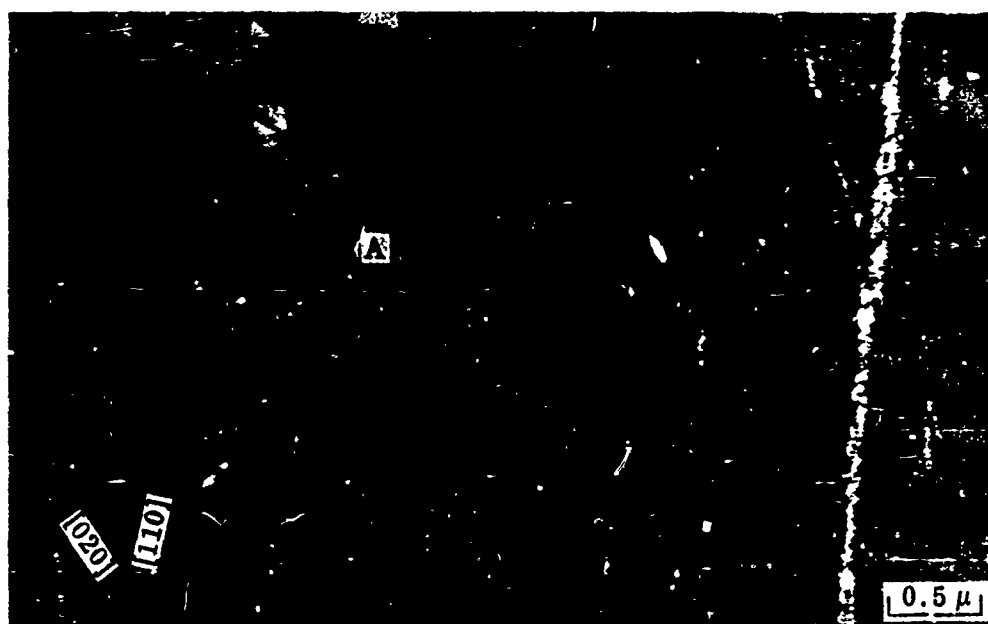
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some oxygen pickup was expected since the gage length of the specimens could not be effectively wrapped. Thus, not only were more precipitates present in the internally oxidized material than in the recovered material before creep testing, but also the longer testing times at 1200°C would be expected to increase the size and volume fraction of precipitates in the internally oxidized alloy.

After 9% creep strain, the networks in the recovered alloys had begun to break up. In the internally oxidized alloy, some networks were seen as well as dislocations outside the networks that were associated with massive precipitates. The structures of both materials appear in Figs. 29 and 30 .

The precipitate at A in Fig. 29a was identified as monoclinic zirconium oxide using selected area diffraction. From this diffraction pattern it was also found that the (011) matrix planes were parallel with the (021) zirconium oxide planes, similar to the case reported in Section 3.2.2.

This examination indicates that in the recovered material steady state creep is associated with the formation of dislocation networks, while in the tertiary stage these networks appear to become unstable and break up. The presence of the precipitate in the prestrained-internally oxidized alloy inhibits dislocation movement and network formation. Networks apparently form at a later stage of secondary creep (> 2% strain), since observations made during tertiary creep indicate networks breaking up

3.4 RECRYSTALLIZATION BEHAVIOR OF Cb-1W-1Zr

Hardness measurements and optical metallography were employed in a study of the recrystallization behavior of prestrained (ϵ = 10%), prestrained-recovered (800°C for 100 hr), and prestrained-internally oxidized (800°C for 100 hr) specimens of Cb-1W-1Zr.

The increase in hardness as a result of the 10% prestrain and the subsequent change in hardness during annealing were too small to allow the recrystallization temperature to be determined with sufficient precision. Moreover, in the case of the internally oxidized

(a) Dislocations Associated With Zirconium Oxide Precipitates (e.g., at A)

(b) Dislocation Network Possibly in Early Stages of Breakup

Fig. 29 Cb-1W-1Zr Prestrained-Internally Oxidized for 100 hr at 800°C
Then Creep Tested to 9% Strain at 1200°C

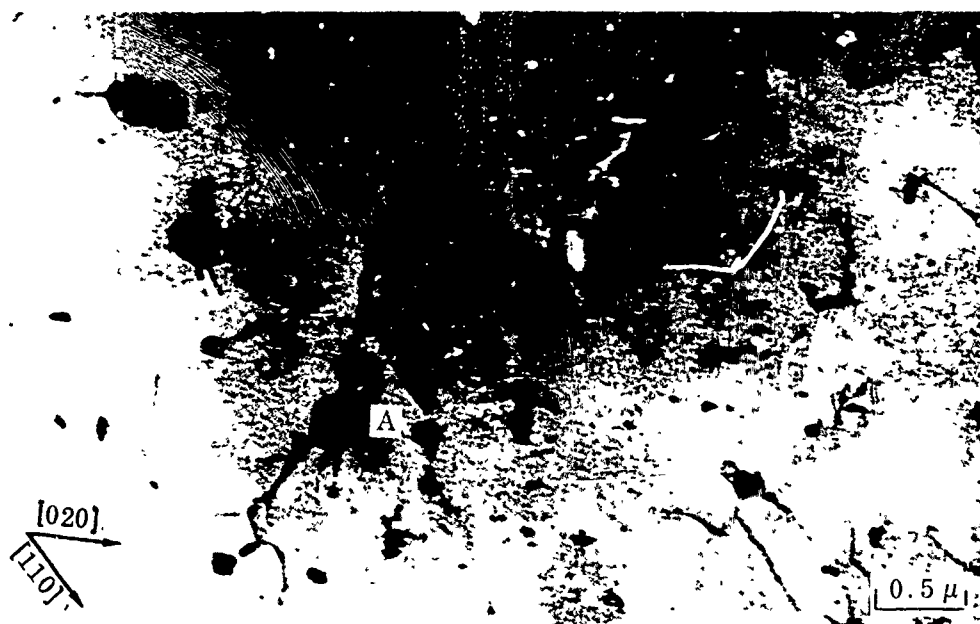(a) Dislocations Associated With Zirconium Oxide Precipitates (e.g., at A)

(b) Dislocation Network Possibly in Early Stages of Breakup

Fig. 29   Cb-1W-1Zr Prestrained-Internally Oxidized for 100 hr at 800°C
Then Creep Tested to 9% Strain at 1200°C

(a) Dislocation Network Breakup

(b) Network Breakup Almost Complete

Fig. 30   Cb-1W-1Zr Prestrained-Recovered 100 hr at 800°C Then Creep
Tested to 9% Strain at 1200°C

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material the hardness values were affected by changes in the precipitate morphology
during annealing. However, metallographic techniques were developed that permitted
the recrystallization temperatures to be established with considerable accuracy.
Dislocation rearrangements, which occurred prior to recrystallization, were observed
by means of dislocation etch pitting.

Figure 31 shows a photomicrograph of the prestrained Cb-1W-1Zr alloy. In some
grains a large number of randomly arranged etch pits were observed. Other grains
were not as favorably oriented for chemical attack, and therefore did not exhibit as
great a degree of etch pitting. Upon annealing the prestrained Cb-1W-1Zr alloy at a
sufficiently high temperature, a regular array of etch pits was revealed as shown in
Figs. 32 and 33 . Annealing at a still higher temperature resulted in the elimination
of such regular dislocation arrays from all grains, indicating that complete recrystal-
lization had taken place. The photomicrograph shown in Fig. 34 reveals this situation
for the prestrained alloy annealed at 14! 0°C for 1 hr. However, the recrystallization
temperature for the prestrained alloy was taken as 1400°C, since the one grain dis-
playing a regular array of etch pits shown in Fig. 33 was the only such grain found
in the entire metallurgical section examined.

Photomicrographs of recovered and internally oxidized specimens showed the same
general features as those observed for the prestrained alloy. Figure 35 illustrates
etch pit arrays in a number of grains in the recovered alloy after annealing at 1400°C
for 1 hr. Annealing this material at 1450°C for 1 hr eliminated all such arrays. Thus,
the recrystallization temperature for the alloy in this condition was between 1400 and
1450°C. Figure 36 shows a photomicrograph of the internally oxidized alloy after
being annealed at 1500°C for 1 hr. The only new feature revealed in this figure is
the presence of a precipitate believed to be zirconium oxide. No arrays of etch pits
were observed in the prestrained-internally oxidized specimen heated to 1550°C for
1 hr, indicating the recrystallization temperature was between 1500 and 1550°C.
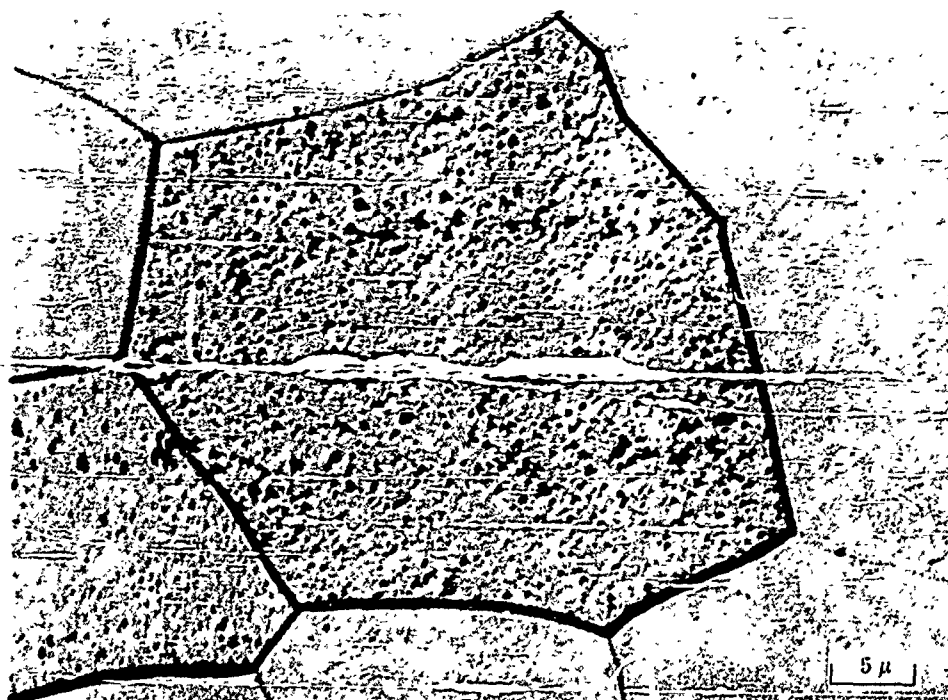
Fig. 31 Cb-1W-1Zr Alloy, Prestrained 10%

Fig. 32 Cb-1W-1Zr Alloy, Prestrained 10%, Then Annealed at 1350°C for 1 hr
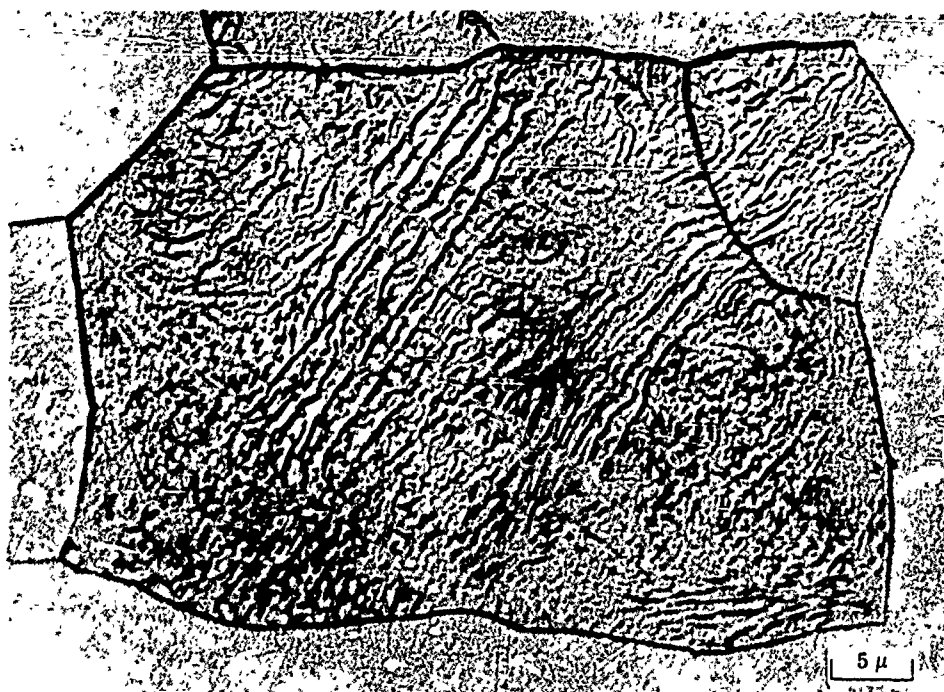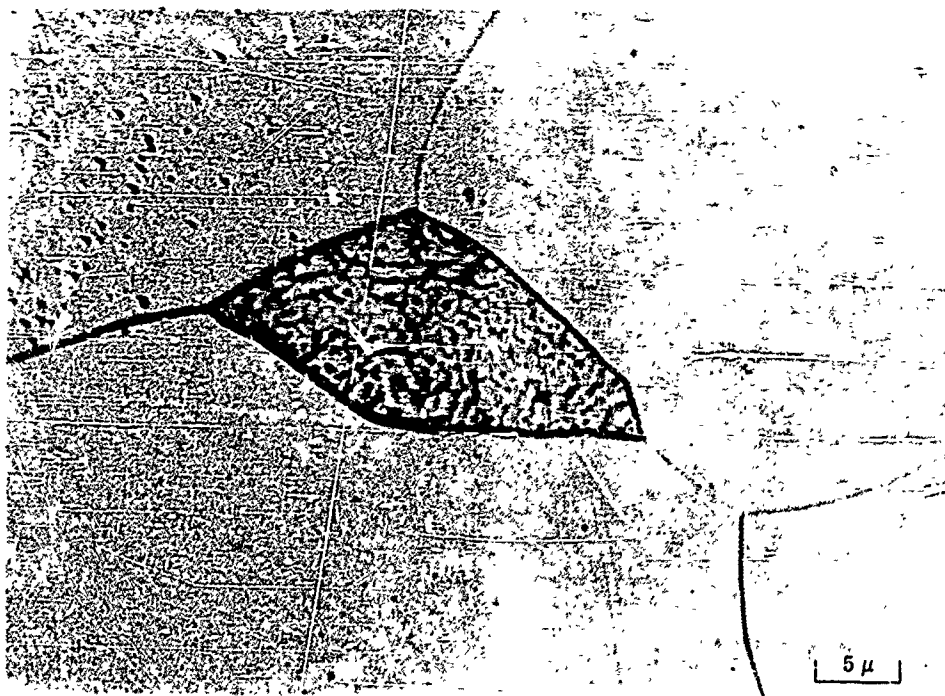
Fig. 33   Cb-1W-1Zr Alloy, Prestrained 10%, Then Annealed at 1400°C for 1 hr

Fig. 34   Cb-1W-1Zr Alloy, Prestrained 10%, Then Annealed at 1450°C for 1 hr
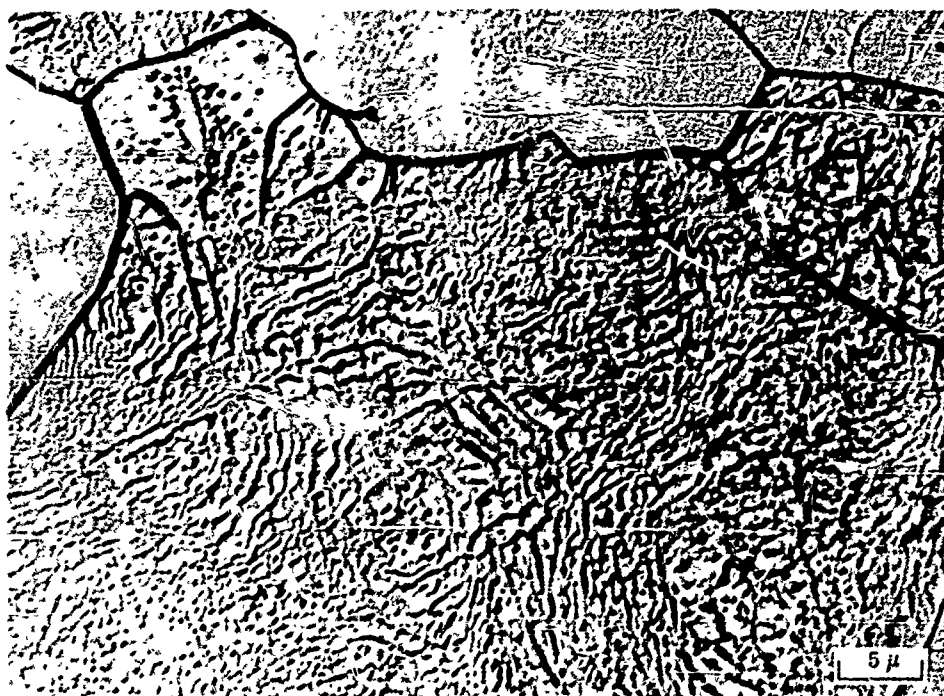
Fig. 35   Cb-1W-1Zr Alloy, Prestrained-Recovered (800°C for 100 hr), Then
Annealed at 1400°C for 1 hr
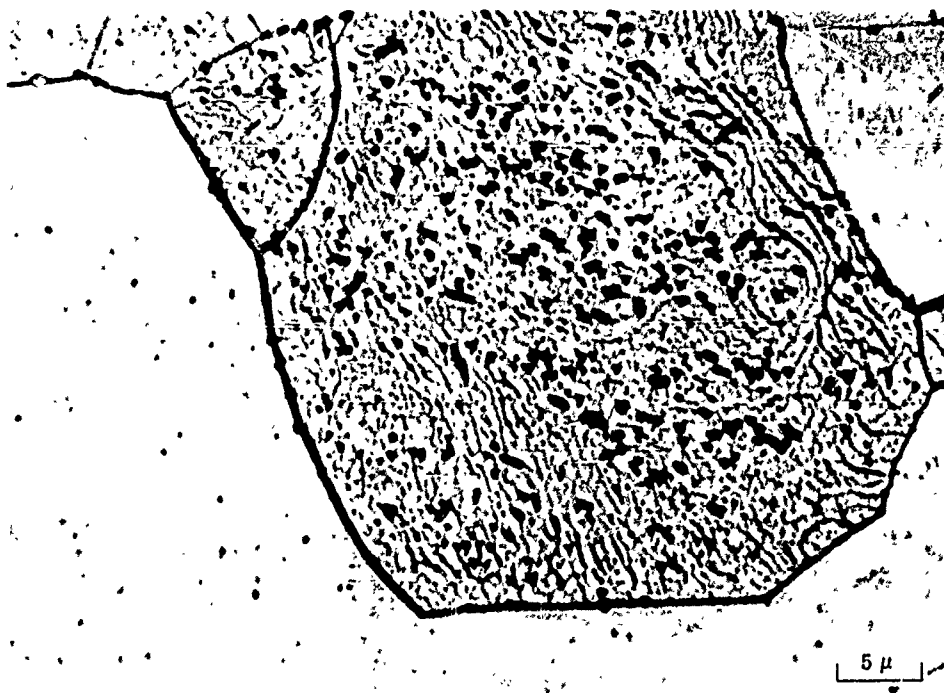
Fig. 36   Cb-1W-1Zr Alloy, Prestrained-Internally Oxidized (800°C for 100 hr),
Then Annealed at 1500°C for 1 hr

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Table 5 summarizes the various alloy conditions and the respective recrystallization temperatures. The recovery treatment at 800°C resulted in a slight increase (less than 50C°) in the recrystallization temperature, suggesting that a more stable substructure with a reduction in strain energy was developed during recovery. The internal oxidation treatment was more effective than the recovery treatment in increasing the recrystallization temperature. This larger increase can be attributed to the formation of zirconium oxide. The fine zirconium oxide precipitates impede dislocation climb and are more effective in retarding recrystallization than the dislocation substructure resulting from the recovery treatment.

Table 5

RECRYSTALLIZATION TEMPERATURES FOR THE Cb-1W-1Zr ALLOY IN VARIOUS CONDITIONS

Alloy Condition	Recrystallization Temperature (1-hr Anneal)
Prestrained, ϵ = 10%	1400°C
Prestrained-Recovered (800°C for 100 hr)	1400−1450°C
Prestrained-Internally Oxidized (800°C for 100 hr)	1500−1550°C

Section 4
SUMMARY

1. The recovery behavior of unalloyed columbium, in terms of f_r, was qualitatively similar to that of the Cb-1W alloy. However, the alloy exhibited a greater degree of recovery than unalloyed columbium though the strengths of the alloy were always higher, due to the solid solution strengthening effect.

2. Recovery in unalloyed columbium and Cb-1W was accompanied by the reappearance of a yield point. The magnitude of the effect increased with increasing annealing time and temperature. This strain-aging effect is thought to be due to oxygen.

3. The recovery behavior of Cb-1Zr was almost identical with that of Cb-1W-1Zr and this behavior was significantly different from that of the unalloyed columbium and the Cb-1W alloy. Some hardening was thought to occur at 800°C due to the formation of zirconium-oxygen zones, while at higher temperatures any precipitates which formed were coarse and not as effective.

4. Strain aging was observed in the Cb-1Zr and Cb-1W-1Zr alloys; this effect decreased with increasing recovery time and temperature. Oxygen atoms are believed to be responsible for strain aging, but during recovery they eventually reach stable sites adjacent to zirconium atoms.

5. Generally, high-purity columbium, Cb-1W, Cb-1Zr, and Cb-1W-1Zr alloys all achieved higher strengths after straining and internal oxidation than after straining and recovery. This strengthening was due to the formation of zirconium-oxygen precipitates.

6. The development of zones and fine precipitates at dislocations in Cb-1W-1Zr, after internal oxidation at 800°C, restricted the rearrangement of dislocations, which normally occurs during recovery.

7. The yield strength and ultimate tensile strength of recrystallized Cb-1W-1Zr was doubled as a result of internal oxidation at 800°C for 100 hr. The yield point was eliminated during this treatment.

8. Internal oxidation of Cb-1W-1Zr at 800°C and 900°C produced coherent zones less than 100 Å in size. These zones are thought to be composed of zirconium-oxygen atoms.

9. The creep resistance of the Cb-1W-1Zr alloy at 1200°C was increased by more than one hundred times as a result of internal oxidation treatments at 800°C.

10. The zones produced at 800°C were no longer present after treatment at 1200°C. Instead large precipitates of monoclinic zirconium oxide were formed.

11. Steady state creep of recovered Cb-1W-1Zr alloys was associated with the formation of dislocation networks, while in tertiary creep these networks were observed to be breaking up.

12. The presence of fine precipitates in the prestrained-internally oxidized Cb-1W-1Zr alloy inhibited dislocation motion during creep. Consequently, dislocation networks form at a later stage of steady state creep deformation than in the case of the prestrained-recovered alloy.

13. The structure consisting of coherent zones developed during internal oxidation was more effective in increasing the recrystallization temperature of Cb-1W-1Zr than the dislocation substructures developed during recovery treatments.

Section 5

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13 ABSTRACT

The effects of recovery and internal oxidation treatments on high-purity columbium, Cb-1W, Cb-1Zr, and Cb-1W-1Zr alloys were investigated in terms of tensile properties. Dislocation arrangements developed in the ternary alloy were examined by thin film transmission electron microscopy. The tensile properties of the Cb-1W-1Zr at room temperature, creep properties at $1200^{\circ}C$, and the recrystallization temperature were determined for the alloy after various treatments.

The recovery behavior of the unalloyed columbium was comparable to that of the Cb-1W alloy. However, the two alloys containing zirconium showed somewhat different behavior due to hardening which was thought to be a result of an interaction between the zirconium atoms and oxygen impurities present in the original sheet.

Transmission electron microscopy revealed that precipitates develop at dislocations during internal oxidation of Cb-1W-1Zr at $800^{\circ}C$ for times in excess of 20 hr. In the as-recrystallized alloy, internal oxidation for 100 hr at $800^{\circ}C$ produced an extremely high density of coherent zones, while at 900 C larger zones were produced. Zones produced at $800^{\circ}C$ were not stable at $1200^{\circ}C$ where large precipitates of monoclinic zirconium oxide were produced.

(CONTINUED)

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The yield and ultimate tensile strengths of recrystallized Cb-1Zr and Cb-1W-1Zr were doubled by internal oxidation treatments at 800°C. In this condition the creep rupture life of the ternary alloy at 1200°C was twenty times that of the as-recrystallized alloy. For short time tests at 1200°C, the recovered Cb-1W-1Zr alloy showed a higher creep resistance than the alloy in the strained or recrystallized conditions.

Structures developed in the Cb-1W-1Zr alloy by internal oxidation were found to be more effective in raising the recrystallization temperature than those developed by recovery treatments.